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VOLATILE ORGANICS IN AERATION GASES AT MUNICIPAL TREATMENT PLANTS

by

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16. ABSTRACT

Utilizing previously developed and validated analytical methods, research was conducted to: (1) estimate volatile (purgeable) Priority Pollutants stripped from aeration basins at a Municipal Wastewater Treatment Facility; (2) determine the volatile Priority Pollutants in wastewater and activated sludge of a treatment facility; (3) determine the equilibrium distribution of volatile Priority Pollutants between the solid and aqueous phases for wastewater and activated sludge; (4) measure volatile pollutants produced by stabilization of sludge by superchlorination; and (5) determine, if any, the chlorinated organics produced during superchlorination of sludge. Liquid and gas sampling strategies were developed to obtain representative data on the emission of purgeable Priority Pollutants from aeration basins of a municipal wastewater treatment facility.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

A knowledge of the fate of volatile organic pollutants as they pass through the wastewater treatment process is necessary to evaluate the final effect of these pollutants on the environment. This report presents the results of a study which quantifies, and defines the fate of these pollutants as they pass through the activated sludge process, and measures the amount of these pollutants produced by superchlorination of sludge. The data generated will be useful in evaluating and controlling the environmental impact of these pollutants.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

Utilizing previously developed and validated analytical methods, research was conducted to: (1) estimate volatile (purgeable) Priority Pollutants stripped from aeration basins at a Municipal Wastewater Treatment Facility; (2) determine the volatile Priority Pollutants in wastewater and activated sludge of a treatment facility; (3) determine the equilibrium distribution of volatile Priority Pollutants between the solid and aqueous phases for wastewater and activated sludge; (4) measure volatile pollutants produced by stabilization of sludge by superchlorination; and (5) determine, if any, the chlorinated organics produced during superchlorination of sludge. Liquid and gas sampling strategies were developed to obtain representative data on the emission of purgeable Priority Pollutants from aeration basins of a municipal wastewater treatment facility.

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SECTION 1

INTRODUCTION

Until this program was initiated a paucity of data was available on the composition and levels of volatile organics in off-gas from aeration basins of wastewater treatment facilities. In fact, a method did not exist for the sampling and analysis of volatile organics in the off-gases until EPA sponsored a program for its development (Contract No. 68-03-2681). The need to know the Priority Pollutant burden in the gases emitted from grit chambers and aeration basins is important since it could have an impact on air quality near wastewater treatment facilities. This research program addressed the question of how the levels of Priority Pollutants which are released into the ambient air can be measured. Essentially there are two ways that can be employed to measure the emissions of Priority Pollutants due to air stripping in grit chambers and aeration basins for activated sludge. The first utilizes the direct sampling of the off-gas and quantifying the volatile organic components collected in these samples. The second utilizes an indirect measurement method in that the volatile organic compounds are measured in the liquid and by using the Henry's Law relationship, an estimation of the vaporization of the compounds of interest is made. In order to utilize the Henry's Law relationship, it is necessary to know the mass transfer coefficient. In activated sludge basins the potential sorption of volatile organics to solids may affect the mass transfer coefficient and thus complicate the use of a simple Henry's Law relationship. Information which provides an insight to the measurement of emissions as a result of off-gassing from aeration basins has been obtained in this research program. The effect of sorption of volatile organics to the solids in activated sludge was also examined.

Because the sludge cake generated from superchlorination of sludge can eventually be delivered to a landfill or used as fertilizer, it is also important to know whether potentially toxic materials are generated by this process. Little information is available on the chemical characterization of chlorinated sludge, and since the process is in operation at some wastewater treatment facilities a characterization study was conducted.

This report describes the results obtained in these two major areas of investigation.

SECTION 2

CONCLUSIONS

^{14}C-Radiolabeled chlorobenzene, toluene, benzene, chloroform, trichloroethylene, carbon tetrachloride and bromobenzene were used to determine the extent of sorption by the solids in activated sludge and raw wastewater. The Freundlich Adsorption Isotherm relationship was used to describe the sorption capacity and intensity of the solid for each of the radiolabeled compounds. Measurable sorption capacities (K) were detected for each of the Priority Pollutants. Sorption studies conducted over several different time periods indicated large variations in K values, *e.g.*, for chloroform it ranged from 0.62 to 3.54. The sorption intensity (n) for several chemicals varied by as much as a factor of 3. The results indicated that the sorption of volatile chemicals to the solid phase in activated sludge cannot be ignored when attempting to predict their concentration in the off-gas by using liquid phase concentrations. The sorption capacity for the same chemicals to solids in raw wastewater was deemed negligible.

A pilot study and two experiments were conducted on different days to determine the levels of volatile Priority Pollutants in the off-gas from aeration basins and in activated sludge and raw wastewater at the Northside Treatment plant in Durham, NC. Methylene chloride, 1,1-dichloroethane, *trans*-1,2-dichloroethylene, chloroform, 1,2-dichloroethane, carbon tetrachloride, bromodichloromethane, trichloroethylene, benzene, tetrachloroethylene, toluene, *o*-dichlorobenzene, and *m*-dichlorobenzene were detected in the off-gas. In general, the concentrations of Priority Pollutants were higher at the front end of the aeration basin than either the middle or end of the basin. In general, a decrease by a factor of 2 to 3 was observed. In contrast the levels of Priority Pollutants measured in the activated sludge did not appear to decrease at the same three points across the aeration basin. The concentrations of Priority Pollutants in raw wastewater were higher, however, than in the activated sludge itself indicating that the Priority Pollutants were partially lost at other points in the treatment facility or that a dilution had occurred prior to reaching the aeration basin. Since significant sorption for the Priority Pollutants to the solid in activated sludge and the lack of a concentration gradient across an aeration basin was observed, it was concluded that the use of liquid phase concentrations to predict the off-gas concentrations for the same Priority Pollutants cannot be accomplished accurately using a simple Henry's Law relationship.

The emission rate from the entire composite aeration tank area for the Northside Treatment Plant in Durham, NC was determined for a number of Priority Pollutants. Four Priority Pollutants exhibited emission rates >1 kg/h. The highest rates were observed for chloroform and tetrachloroethylene with emission reaching 5.7 kg/h and 7.0 kg/h, respectively.

Sampling and analysis for chlorinated compounds in superchlorinated sludge revealed the presence of several hundred chlorinated constituents. The measurement of organic chlorine in the solid phase from the effluent of superchlorinated sludge indicated the presence of 2 to 4 1/2% organic chlorine. The organic chlorine content for the influent was not detectable using the Schöniger method. The application of negative ion chemical ionization/mass spectrometry (NICI/MS) greatly facilitated the specific and sensitive detection of chlorinated compounds. Quantification of purgeable Priority Pollutants prior to and after chlorination of sludge indicated increases in their concentrations. Chloroform increased from ∿6 ppb to over 1,000 ppb before and after chlorination of sludge, while carbon tetrachloride was not detected in the influent and was measured at levels upto 989 ppb in the chlorinated sludge effluent. Increases of almost three orders of magnitude were also observed for *p*-chlorotoluene, in some cases from only trace levels to 1,620 ppb. Likewise analysis of acid, base and neutral fractions utilizing the Priority Pollutant method for sludge analysis yielded only a few chlorinated nonpriority pollutants in these fractions. In contrast the examination of the "discard" fraction generated by this method by NICI/MS indicated that the majority of the chlorinated compounds were contained in these fractions which were amenable to gas chromatography. Even though quantification of the chlorinated compounds detected by NICI/MS was not conducted, it was evident that a major portion of the chlorinated organics was not detected by this method since the Schöniger method had demonstrated the presence of up to 4-1/2% organic chlorine in the solid component of the chlorinated sludge.

SECTION 3

RECOMMENDATIONS

Since this research program indicated that substantial levels of volatile Priority Pollutants are present in the off-gas from aeration basins, it is recommended that additional studies be conducted with other wastewater treatment facilities. Wastewater treatment facilities that receive predominantly industrial and municipal wastewater should be investigated since the facility investigated here receives 40% industrial/60% municipal sewage.

Additional research is needed to determine the identity of chlorinated organics produced via superchlorination of sludge. Since approximately 3% of the organics in effluent sludge from a superchlorination process was chlorinated and only a small fraction was detected by capillary GC/NICI-MS/COMP, it is recommended that the non-volatile fraction be characterized by ancillary techniques. Very little information exists concerning the identity, toxicity, and mutagenicity of the chlorinated organics.

SECTION 4

PROGRAM OBJECTIVES

This research program, the first of its kind, had the following broad objectives:

(1) confirm the quantitative capabilities of the previously developed and validated sampling apparatus and analytical procedure for measuring volatiles from aeration basins at Wastewater Treatment Facilities;

(2) develop liquid and gas sampling strategies to provide a representative analysis of the loss of volatiles from aeration basins;

(3) consider factors such as geometry, liquid flow pattern, and air flow pattern to determine the optimum sampling strategy;

(4) analyze both liquid and off-gas for volatile Priority Pollutants;

(5) measure equilibrium partition of several compounds between the liquid, solid and gas phase;

(6) conduct sampling and analysis of vapors produced by stabilization of sludge by superchlorination;

and (7) relate concentrations in off-gas to system and wastewater characteristics, if possible.

The results obtained from the research on each of the above objectives would serve to fully verify a field-tested procedure and a body of data relating the concentration of Priority Pollutants in the aeration system off-gas to the system and wastewater characteristics.

SECTION 5

PARTITIONING OF "PURGEABLE" PRIORITY POLLUTANTS BETWEEN AQUEOUS AND SOLID PHASES IN ACTIVATED SLUDGE SAMPLES

INTRODUCTION

It would be desirable to predict the concentration of volatile organics in the off-gas from aeration basins based on the concentrations measured in the liquid phase. Measurements of volatile organics in liquid samples present fewer problems with the mechanics of sample acquisition from the treatment facility. However, in order to successfully predict the concentration of volatiles in the off-gas, it is necessary to recognize and understand the potential equilibria of pollutants between the solid, liquid and gas phases such as in the aeration of activated sludge. Figure 1 depicts the relationships between these three phases and a given input rate of a chemical.

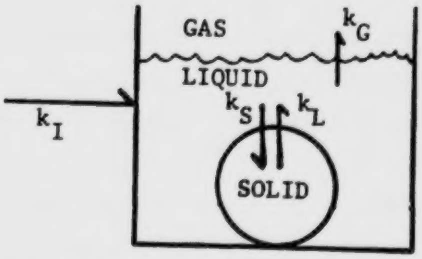


Figure 1. Potential gas-liquid-solid equilibria in aeration basin.

The material balance equation for a chemical in the above schematic of interactions in an aeration basin is given by:

$$V\frac{dC_W}{dt} = k_I - k_S S C_W + k_L S C_S - k_G A C_W \qquad (1)$$

where V = volume of water

A = surface area of the water in the basin

S = weight of the solid

C_W = concentration of the chemical in water

k = rate constants (I = input, S = sorption to solid, L = desorption, G = vaporization)

C_S = concentration of the chemical in the solid

If a chemical has a k_L/k_S ratio >> 1, then the relationship can be simplified to $VdC_W/dt = k_I - k_G AC_W$. Using Henry's Law one can approximate the rate of volatization of the chemical:

$$-\frac{dC_w}{dt} = K_{iL}\,(C_W - P_i/H_i) \qquad (2)$$

where K_{iL} = mass transfer coefficient

P_i = partial pressure of the chemical

H_i = Henry's Law constant

The integrated form of the first-order rate expression allows the calculation of the concentration at a point in time (t):

$$C_{w(t)} = C_{w(o)} e^{-K_{iL}(C_W - P_i/H_i)} \qquad (3)$$

It follows that the concentration of the chemical in the liquid phase should decrease with time of forced air diffusion in a body of liquid such as in the aeration of activated sludge.

A study was conducted to determine the sorption of ^{14}C-labeled Priority Pollutants onto the solids in activated sludge for chloroform, carbon tetrachloride, trichloroethylene, benzene, chlorobenzene and toluene. The purpose of this study was to determine whether there was an insignificant sorption of the Priority Pollutants to the solid sludge so that the simple Henry's Law relationship could be used to approximate the rate of volatilization of Priority Pollutants from activated sludge in aeration basins. Also, the concentrations of Priority Pollutants were measured (Section 6) in the activated sludge at the entrance and exit of an aeration basin to determine whether equation (3) indeed applies.

EXPERIMENTAL

Description of Treatment Plant

The plant selected for characterization of sorption phenomena and the measurement of Priority Pollutant levels in the off-gas was the Northside Treatment Plant in Durham, NC. The Northside Treatment Plant treats raw wastewater from homes, businesses and industries in the northeast side of Durham. It receives approximately 40% industrial and 60% municipal sewage. Typical flow is 0.28 cubic meters/sec. A diagram of this plant is shown in Figure 2. The major units include: (1) coarse screening (mechanical bar screen); (2) grit removal and flotation of grease in a vacuum process (Vacuator); (3) roughing, trickling filtration; (4) primary sedimentation; (5) conventional activated sludge with a 4 to 6 h detention and forced air diffusion (observation of the tanks indicates that the flow pattern is arbitrary somewhere between plug flow and complete vertical and partial lateral mixing); (6) secondary sedimentation with sludge recycle; (7) chlorination; and (8) anaerobic sludge digestion.

The areation tanks are each 4.5 x 60.96 m with a depth of 3.96 m. Liquid depth is ~3.5 m. Air is injected into each tank by 344 porous plates, 30.4 cm x 304 cm, set vertically in double rows in a header placed 30.4 cm above the tank bottom. There is a total of 9 aeration tanks at this facility.

Materials

^{14}C-Radiolabeled chlorobenzene, toluene, benzene, chloroform, trichloroethylene, bromobenzene and carbon tetrachloride were obtained from New England Nuclear (Boston, MA). Scintillation cocktail containing 250 mL of Triton X, 750 mL toluene, and 4.5 g of Omnifluor was prepared. Aliquots of the sample were added to 15 mL of scintillation cocktail and radioactivity was determined on a Packard Tricarb 3375 liquid scintillation spectrometer. The radiotracer was counted until a standard error of 2.5 was obtained. Observed radioactivity was corrected for quenching by the external standard ratio method and all counts/min (CPM) were converted to disintegrations/min (DPM).

Samples

Samples collected for this study are given in Tables 1 and 2 and their locations in Figure 2. Samples were also collected of raw wastewater entering

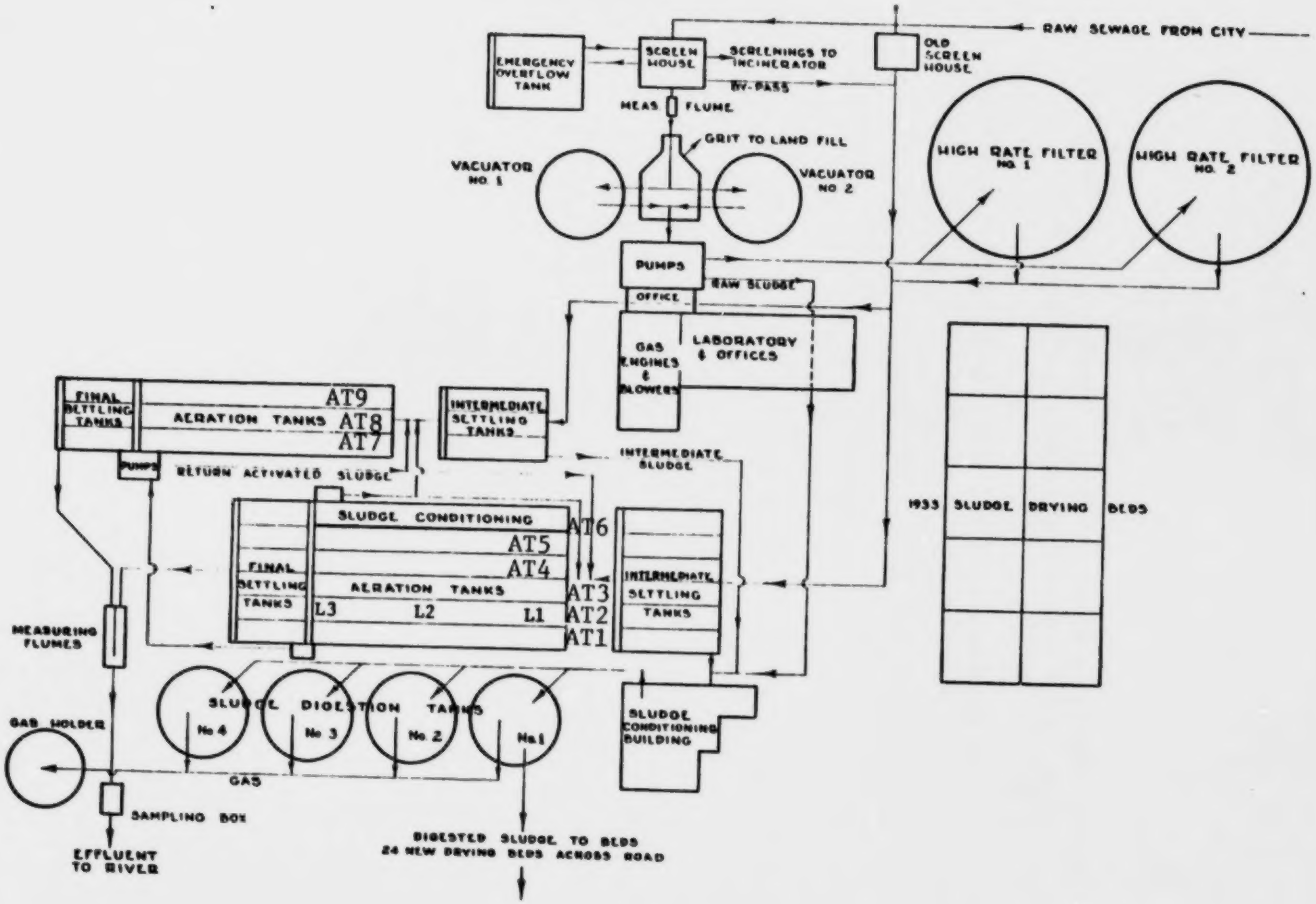

RAW SEWAGE FROM CITY
OLD SCREEN HOUSE
EMERGENCY OVERFLOW TANK
SCREEN HOUSE
SCREENINGS TO INCINERATOR
BY-PASS
MEAS FLUME
GRIT TO LAND FILL
VACUATOR NO 1
VACUATOR NO 2
HIGH RATE FILTER NO. 1
HIGH RATE FILTER NO. 2
PUMPS
RAW SLUDGE
OFFICE
GAS ENGINES & BLOWERS
LABORATORY & OFFICES
1933 SLUDGE DRYING BEDS
FINAL SETTLING TANKS
AERATION TANKS
AT9
AT8
AT7
INTERMEDIATE SETTLING TANKS
PUMPS
RETURN ACTIVATED SLUDGE
INTERMEDIATE SLUDGE
SLUDGE CONDITIONING
AT6
AT5
AT4
AT3
AT2
AT1
FINAL SETTLING TANKS
AERATION TANKS
L3
L2
L1
INTERMEDIATE SETTLING TANKS
MEASURING FLUMES
SLUDGE DIGESTION TANKS
No 4
No 3
No 2
No 1
SLUDGE CONDITIONING BUILDING
GAS HOLDER
GAS
SAMPLING BOX
EFFLUENT TO RIVER
DIGESTED SLUDGE TO BEDS
24 NEW DRYING BEDS ACROSS ROAD

Figure 2. Flow diagram of Northside Treatment Sewage Plant, Durham, NC. (Pilot Study: sampling at L1 and L3 only; Study No. 1: sampling at L1 and L3 only; Study No. 2: sampling at L1, L2 and L3).

Table 1. SAMPLING PARAMETERS FOR ACTIVATED SLUDGE: PILOT STUDY - NORTHSIDE TREATMENT PLANT, DURHAM, NC[a]

Sampling Period No.	Sampling Time
1[b]	1250-1305 h
2	1345-1400 h
3[b]	1505-1525 h
4	1600-1615 h
5[b]	1720-1740 h

[a] Samples taken concurrently with off-gas samples described in Section 6 (Table 11).

[b] Samples collected for sorption studies, other samples also collected for determining "purgeable" Priority Pollutants in activated sludge (see Section 6, Table 11). Samples of sludge were collected from location No. 1 in aeration tank No. 2 (AT2, Fig. 2) on August 19, 1979.

Table 2. SAMPLING PARAMETERS FOR ACTIVATED SLUDGE: STUDY NO. 2 - NORTHSIDE TREATMENT PLANT, DURHAM, NC[a]

Period No.	Location		
	L1	L2	L3
1[b]	1200 h	1210 h	1220 h
2	1300 h	1310 h	1320 h
3[b]	1400 h	1410 h	1420 h
4	1500 h	1510 h	1520 h
5[b]	1600 h	1610 h	1620 h

[a] Samples taken concurrently with off-gas samples described in Section 6 (Table 12).

[b] Samples collected for sorption studies, other samples also collected for determining "purgeable" Priority Pollutants in activated sludge (see Section 6, Table 12). Samples were taken from AT2 (Fig. 2) on January 29, and again on May 14, 1980. Raw wastewater was also collected at 1130 on May 14, 1980.

into the Northside Treatment Plant (Durham, NC) and at specified points of monitoring for Priority Pollutants in aeration gases.

Sampling Materials and Methods

Liquid samples from the aeration basins and the incoming raw wastewater were scooped with a 1 L beaker and transferred via a glass funnel to a 1 L narrow mouth glass amber bottle with Teflon®-lined cap. The glass funnel was washed with deionized-distilled water after each sample duplicate had been collected. All glassware was prewashed with nondetergent soap, rinsed with deionized-distilled water, and dried in an infrared oven and baked in an oven at 450°C for 2 h. Samples collected were placed on ice, transported back to the laboratory and stored at 4°C until ready for use in experiments.

Equilibration Time

In order to determine the time required to achieve equilibrium conditions for Priority Pollutants between the liquid and solid phases, a duplicate study was conducted. One µL of radiolabelled halogenated aromatics in methanol was added to 10 mL of activated sludge and equilibrated for 30 min and 18 h at 4°C with magnetic stirring in 50 mL centrifuge tubes (Teflon®-lined caps). In each experiment, approximately 200 ng of ^{14}C-bromobenzene and 750 ng of ^{14}C-chlorobenzene were used. After equilibration, the solids were removed by slow speed centrifugation (∼500 rpm) and 1.0 mL aliquots of the supernatant were transferred to 15 mL of toluene/Omnifluor/Triton X cocktails and the radioactivity determined. An aliquot of the solids was also measured for radioactivity. The DPMs were normalized against a single measured volume for comparison. Equal amounts of spiking solutions were added to blank cocktails to serve as recovery standards.

Data in Table 3 reflect the disparity in sorption at the low concentration level for the 30 min study. Approximately 65 to 66% of the chlorobenzene and bromobenzene were recovered in the liquid phase after centrifugation and removal of the solid phase. A second experiment was conducted with an equilibration temperature and time of 4° for 18 h, respectively (Table 4). These results indicate that the sorption of chlorobenzene and bromobenzene to the solid phase does not increase with time. Sorption of the Priority Pollutant to the solid phase occurs rather rapidly under the vigorous mixing conditions and an apparent equilibrium is reached between the surface of the

Table 3. ADSORPTION OF CHLOROBENZENE AND BROMOBENZENE TO ACTIVATED SLUDGE[a]

Compound	Percent Recovered ± S.D.	
	Liquid Phase	Solid Phase
Chlorobenzene	66 ± 1.0	34 ± 1.0
Bromobenzene	65 ± 0.5	35 ± 1.0

[a] 30 min equilibration @ 4°C.

[b] Solid phase was 30 mg/mL of total sludge.

Table 4. ADSORPTION OF CHLOROBENZENE AND BROMOBENZENE TO ACTIVATED SLUDGE[a]

Compound	Percent Recovered ± S.D.	
	Liquid Phase	Solid Phase
Chlorobenzene	65	35
Bromobenzene	65 ± 0.5	35 ± 1.0

[a] 18 h equilibration @ 4°C.

[b] Solid phase was 30 mg/mL of total sludge.

solid matrix and liquid phase. However, this study does not indicate whether a very long time period is needed for the sorption of the chlorobenzene or bromobenzene into the micropore structure of the solid matrix. In all subsequent experiments, equilibration was allowed to proceed for 18 h at 4°C to preserve the integrity of the sludge.

Aqueous-Solid Sorption Studies

Measurements of adsorptive properties of a chemical to a solid particle can be described by adsorption isotherms which relate the concentration of the chemical in the aqueous phase (C_w) and the concentration on the solid phase (C_S) at equilibrium. These units may be expressed in μg/L and μg/g. The adsorption of radiolabeled Priority Pollutants to the solids in activated sludge were expressed by the Freundlich equation. The Freundlich adsorption isotherm is an empirical equation which gives the most general description of a variety of relationships:

$$C_S = KC_w^n \text{ or } \log C_S = \log K + n \log C_W \qquad (4)$$

where K (or log K) and n are the important parameters of adsorption strength and shape of the curve. Using double log plots of the measured equilibrium concentrations, the actual values of n and log K can be determined where n is the slope and log K the intercept of the line. When n approaches unity, the amount adsorbed is then proportional to the water concentration. Thus, the magnitude of the intercept is an indicator of adsorption capacity and the slope of adsorption intensity.

The data obtained by measuring the quantity of radiolabeled compounds distributed between the liquid and solid phases were subjected to a linear regression analysis according to the above equation. Each data point for linear regression analysis constituted at a minimum a triplicate determination of the distribution of the radiochemical between the solid and liquid phases.

Effect of Carrier Volume on Sorption--

The effect of the spiking carrier volume on the sorption of benzene to activated sludge was examined at 3 different concentrations of benzene (Table 5). Methanol was the carrier solvent in both cases. Benzene at 1, 100 and 1500 ppb was used in combination with spiking volumes of 50 and 1,000 μL. It is evident from these data that perhaps at low levels, *i.e.*, 1 ppb, the use of excessive amounts of carrier solvent might compete with the

Table 5. EFFECT OF SPIKING CARRIER VOLUME ON FREUNDLICH ADSORPTION ISOTHERM PARAMETERS FOR BENZENE IN ACTIVATED SLUDGE[a]

Spiking Vol. (μL)	Initial Conc. (μg/L)	Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r
50	1	-0.357	0.271	0.774	0.63 (4.27)	0.991
	100	1.732	2.186			
	1500	3.100	2.903			
1000	1	-0.229	0.136	0.861	0.41 (2.57)	0.993
	100	1.771	2.136			
	1500	3.090	2.954			

[a] Samples were taken as part of pilot study - Northside Treatment Plant, Durham, NC (August 19, 1979).

Priority Pollutant for sorption to the solid matrix. Increasing the spiking volume of solvent from 50 to 1000 μL reduced the sorption capacity by 40% (Table 5). In all subsequent experiments, where possible, 50 μL of carrier solvent, methanol, was employed.

The preparation of standard and sample cocktails for this and subsequent experiments was as described above with one modification: aqueous phases were obtained by gravity settling instead of centrifugation.

Normalization of liquid volumes was employed in order to allow for comparing information between experiments. The liquid volume was measured after pipetting a 1.0 mL aliquot to the scintillation cocktail by decanting the remaining supernatant liquid into a graduated cylinder. A net sludge volume of 0.82 ± 0.27 mL was obtained and normalization values were determined by the difference between this value and the spiking volume (9.23 for 50 μL spikes, 10.18 for 1.0 mL volume spikes). A composite (pooled) liquid volume was obtained for 50 μL spiking. The normalization factor was then obtained (9.11) which was not significantly different from the value for previous experiments. Thus, the uncertainties of normalization were not propagated in the sorption studies.

Sorption of Selected Priority Pollutants--

The purpose of these experiments was to determine whether significant changes occurred with time and location within the aeration tanks of the adsorption capacity (and intensity) of activated sludge for Priority Pollutants. If the simple relationship described by equation 3 is to be used for predicting the concentration of Priority Pollutants in the off-gas stream, then the concentration determined in the liquid phase must be relatively independent of sorption to the solid phase. Sorption would perturb the distribution of Priority Pollutants between the liquid and gas phases. It follows that the adsorption capacities and intensities must be relatively small or that the mass transfer coefficient be measured for each case to use eq. 3.

The sorption of several Priority Pollutants to activated sludge as a function of concentration for the Pilot Study is given in Table 6. The various adsorption isotherm parameters have been tabulated for reference. The initial concentration for each of the chemicals is indicated as well as

Table 6. FREUNDLICH ADSORPTION ISOTHERM PARAMETERS: SELECTED PRIORITY POLLUTANTS IN ACTIVATED SLUDGE - PILOT STUDY AT NORTHSIDE TREATMENT FACILITY, DURHAM, NC

Compound	Initial Conc. µg/L	Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r
Chloroform	1.1	-0.119	0.060	0.532	-0.06 (0.87)	0.748
	10.9	1.037	0			
	54.4	1.699	1.161			
Benzene	2.0	-0.009	0.531	0.957	0.55 (3.5)	0.999
	48.9	1.379	1.920			
	99.6	1.739	2.174			
Chlorobenzene	1.9	0.027	0.445	0.747	0.44 (2.75)	0.995
	48.8	1.540	1.674			
	97.6	1.898	1.791			
Toluene	2.0	0.121	0.355	1.036	0.29 (1.94)	0.973
	49.8	1.369	1.944			
	99.6	1.791	1.968			

K expressed as ug/g of dry sludge solids. Sludge concentration 0.3 g/l.

log C_W, log C_S, the slope (n), intercept (log K, K) and the correlation coefficient for the linear regression. The initial concentration chosen for all of the sorption studies was based on preliminary data on levels of Priority Pollutants in activated sludge (1). These levels were generally 1 to 100 ppb.

Of the four chemicals employed in this study, benzene exhibited the highest adsorption capacity (K = 3.5). It is interesting to compare this value with that found for its adsorption to carbon where the reported K value was 1 (2). In contrast the K value for chloroform was considerably less than that reported for its adsorption to carbon. The adsorption capacity of chlorobenzene and toluene for carbon is reported as 91 and 26, respectively (2). A comparison of the K values for carbon with activated sludge indicates that the adsorption capacity is considerably lower in activated sludge.

In the first of two experiments, 10 mL of each total sludge sample was pipetted into a 50 mL centrifuge tube containing a magnetic stirrer. The sludge was magnetically stirred to provide good mixing of the sample. Fifty µL of radioisotope in methanol solution was pipetted directly onto the surface interface such that initial concentrations of 5, 50 and 100 ppb were achieved (0.05, 0.50, and 1.0 µg/10 mL). The tubes were then sealed with glass stoppers or Teflon®-lined caps and transferred to a cold room at 4°C. The samples were stirred for 16 h, pipetted into 15 mL graduated conical centrifuge tubes and let stand for 2 h. Aliquots were then transferred to a Triton X/toluene/Omnifluor scintillation cocktail for counting of the radioisotope. The solid volume was recorded to ±0.05 mL to obtain the total liquid volume necessary for the normalization of the scintillation radioisotopic data.

The results for aqueous-solid sorption experiment No. 1 for activated sludge are given in Table 7. The adsorption isotherm parameters for the selected Priority Pollutants were determined at time periods 1 and 2 (see Table 2) at three locations in the aeration tank No. 2 (see Figure 1). All data were results of triplicate analysis for each concentration, period, and location. The data in Table 7 indicate significant differences in the adsorption capacity for Priority Pollutants both with respect to time and

Table 7. FREUNDLICH ADSORPTION ISOTHERM PARAMETERS FOR SELECTED PRIORITY POLLUTANTS IN ACTIVATED SLUDGE: NORTHSIDE TREATMENT PLANT, DURHAM, NC - EXPERIMENT NO. 1

Compound	Period	Location	Initial Conc. μg/L	Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r
Chloroform	1	1	5.0	0.432	0.894	1.002	0.55 (3.54)	0.961
			49.8	1.253	2.026			
			99.5	1.746	2.164			
	1	2	5.0	0.512	0.766	1.057	0.20 (1.58)	0.988
			49.8	1.536	1.711			
			99.5	1.754	2.154			
	1	3	4.6	0.441	0.788	0.828	0.41 (2.57)	0.998
			46.1	1.521	1.634			
			92.2	1.797	1.935			
	2	1	5.0	0.455	0.855	0.890	0.48 (3.02)	0.987
			49.8	1.438	1.873			
			99.5	1.783	1.983			
	2	2	5.0	0.498	0.894	0.921	0.46 (2.88)	0.992
			49.8	1.438	1.873			
			99.5	1.811	2.065			
	2	3	4.6	0.538	0.583	1.435	-0.21 (0.62)	0.985
			46.1	1.470	1.743			
			92.2	1.608	2.236			
Carbon tetrachloride	1	1	5.0	-0.154	1.156	0.929	1.38 (23.9)	0.969
			49.8	0.651	2.179			
			99.5	1.253	2.435			
	1	2	5.0	0	1.125	1.020	1.11 (12.9)	0.993
			49.8	1.059	2.107			
			99.5	1.228	2.440			
	1	3	4.6	0.231	0.985	1.458	0.70 (5.01)	0.912
			46.1	1.111	2.044			
			92.2	0.965	2.442			

(continued)

Table 7 (cont'd.)

Compound	Period	Location	Initial Conc. µg/L	Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r
	2	1	5.0 49.8 99.5	-0.046 0.697 1.320	1.186 2.174 2.418	0.915	1.32 (20.9)	0.960
	2	2	5.0 49.8 99.5	0.061 0.901 1.396	1.108 2.144 2.396	0.993	1.10 (12.6)	0.982
	2	3	4.6 46.1 92.2	-0.161 0.942 1.243	1.115 2.095 2.396	0.905	1.26 (18.2)	0.999
Chlorobenzene	1	1	5.0 49.8 99.5	0.447 1.468 1.489	0.865 1.833 2.360	1.201	0.32 (2.09)	0.944
	1	2	5.0 49.8 99.5	0.243 1.438 1.776	1.035 1.873 2.123	0.707	0.86 (7.24)	0.999
	1	3	4.6 46.1 92.2	0.441 1.420 1.784	0.788 1.820 2.019	0.945	0.39 (2.45)	0.993
	2	1	5.0 49.8 99.5	0.362 1.253 1.705	0.954 2.026 2.211	0.973	0.65 (4.47)	0.980
	2	2	5.0 49.8 99.5	0.484 1.277 2.761	0.813 2.012 2.144	0.521	0.87 (7.41)	0.821
	2	3	4.6 46.1 92.2	0.476 1.255 1.672	0.730 1.972 2.178	1.260	0.19 (1.55)	0.976

(continued)

Table 7 (cont'd.)

Compound	Period	Location	Initial Conc. µg/L	Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r
Toluene	1	1	5.0 49.8 99.5	0.114 1.360 1.600	1.091 1.953 2.299	0.773	0.99 (9.77)	0.991
	1	2	5.0 49.8 99.5	0.423 1.413 1.688	0.894 1.901 2.228	1.045	0.45 (2.82)	0.999
	1	3	4.6 46.1 92.2	0.419 1.379 1.672	0.819 1.868 2.178	1.087	0.36 (2.29)	0.999
	2	1	5.0 49.8 99.5	0.398 1.378 1.542	0.921 1.936 2.334	1.166	0.44 (2.75)	0.990
	2	2	5.0 49.8 99.5	0.255 2.396 1.736	1.028 1.919 2.245	0.484	1.022 (10.5)	0.843
	2	3	4.6 46.1 92.2	0.335 1.243 1.618	0.910 1.979 2.228	1.055	0.58 (3.80)	0.994
Benzene	1	1	5.0 49.8 99.5	0.431 1.202 1.144	0.885 2.053 2.455	1.805	0.13 (1.35)	0.950
	1	2	5.0 49.8 99.5	0.455 1.421 1.776	0.855 1.369 1.599	0.557	0.59 (3.89)	0.999
	1	3	4.6 46.1 92.2	0.419 1.380 1.672	1.130 1.919 2.314	0.914	0.73 (5.37)	0.994

(continued)

Table 7 (cont'd.)

Compound	Period	Location	Initial Conc. µg/L	Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r
	2	1	5.0 49.8 99.5	0.255 1.429 1.722	1.028 1.883 2.193	0.775	0.82 (6.61)	0.997
	2	2	5.0 49.8 99.5	0.477 1.241 1.516	0.824 2.033 2.347	1.491	0.13 (1.35)	0.988
	2	3	4.6 46.1 92.2	0.403 1.435 1.618	0.839 1.799 2.228	1.071	0.39 (2.45)	0.986
Trichloroethylene	1	1	5.0 49.8 99.5	-0.155 1.077 1.413	1.156 2.101 2.390	0.782	1.27 (18.6)	0.999
	1	2	5.0 49.8 99.5	0.615 1.331 1.621	1.021 1.976 2.284	1.270	0.25 (1.78)	0.999
	1	3	4.6 46.1 92.2	0.344 1.220 1.577	0.902 1.919 2.258	1.111	0.53 (3.39)	0.999
	2	1	5.0 49.8 99.5	0.079 1.202 1.631	1.103 2.053 2.277	0.775	1.05 (11.2)	0.996
	2	2	5.0 49.8 99.5	0.491 1.310 1.475	0.802 1.991 2.366	1.545	0.03 (1.07)	0.997
	2	3	4.6 46.1 92.2	0.254 1.079 1.618	0.971 2.056 2.228	0.954	0.81 (6.46)	0.962

K expressed as ug/g of dry sludge solids. Sludge concentration 0.3 g/l.

location in the aeration tank. For example, the variations in the K values for chloroform ranged from 0.62 to 3.54. Data for other Priority Pollutants (Table 8) show similar trends. Also, the sorption intensity (n) for several chemicals varies by as much as a factor of 3.

In order to more clearly demonstrate this variation, the mean value, standard deviation, and coefficient of variation were calculated for the sorption intensity (n) and sorption capacity (K) for time periods 1 and 2 of experiment No. 1. These data are given in Table 8. Inspection of the coefficients of variation (given in parenthesis) for each chemical's mean value of n and K indicates a large variation within the three sampling locations of aeration tank No. 2. Table 9 gives the variation of the adsorption isotherm parameters for all data listed in Table 8. Although the statistical accuracy for the adsorption intensity and capacity of these selected Priority Pollutants for the solids in activated sludge is greater than the individual data given in Table 8, the variation as expressed by the coefficient of variation is large. These results probably imply that the sorption of volatile chemicals to the solid phase in activated sludge cannot be ignored when attempting to predict their concentration in the off-gas by using liquid phase concentrations.

A comparison of the adsorption isotherm parameters for raw wastewater with activated sludge clearly indicates that the adsorption capacity for the chemicals studied is negligible in raw wastewater (Table 10). The sorption intensity for benzene, chlorobenzene, chloroform and toluene for activated sludge in experiment No. 2 is comparable to the values observed in previous experiments. A slightly larger disparity in the K values was observed between the two sets of data (compare Tables 6 and 10).

Table 8. VARIATION OF FREUNDLICH ADSORPTION ISOTHERM PARAMETERS FOR SELECTED PRIORITY POLLUTANTS IN ACTIVATED SLUDGE[a]

Compound	Period 1		Period 2	
	n	K	n	K
Chloroform	0.962 ± 0.119 (12)	2.40 ± 1.51 (63)	1.082 ± 0.306 (28)	1.74 ± 2.45 (141)
Carbon tetrachloride	1.136 ± 0.283 (25)	11.5 ± 2.19 (19)	0.938 ± 0.048 (5)	16.9 ± 1.29 (8)
Chlorobenzene	0.951 ± 0.247 (26)	3.31 ± 1.95 (60)	0.918 ± 0.373 (41)	3.71 ± 2.24 (60)
Toluene	0.968 ± 0.170 (18)	3.98 ± 2.19 (55)	0.902 ± 0.366 (41)	4.78 ± 1.99 (42)
Benzene	1.092 ± 0.643 (59)	3.02 ± 2.04 (68)	1.112 ± 0.360 (32)	2.82 ± 2.24 (79)
Trichloroethylene	1.054 ± 0.249 (24)	4.79 ± 3.39 (71)	1.091 ± 0.403 (37)	4.27 ± 3.47 (81)

[a] Mean values ± S.D. (C.V.) for n and K were calculated for locations 1 through 3 in Table (7).

Table 9. VARIATION OF FREUNDLICH ADSORPTION ISOTHERM PARAMETERS FOR SELECTED PRIORITY POLLUTANTS IN ACTIVATED SLUDGE - MEAN ± S.D. (C.V.) FOR ALL DATA IN TABLE 7

Compound	n	k
Chloroform	1.022 ± 0.218 (21)	2.04 ± 1.91 (93)
Carbon tetrachloride	1.037 ± 0.211 (20)	13.8 ± 1.74 (13)
Chlorobenzene	0.934 ± 0.283 (30)	3.54 ± 1.95 (55)
Toluene	0.935 ± 0.258 (28)	4.36 ± 1.95 (45)
Benzene	1.102 ± 0.466 (42)	2.88 ± 1.99 (69)
Trichloroethylene	1.073 ± 0.300 (28)	4.57 ± 3.02 (66)

Table 10. COMPARISON OF FREUNDLICH ADSORPTION ISOTHERM PARAMETERS FOR SELECTED PRIORITY POLLUTANTS IN RAW WASTEWATER INFLUENT WITH ACTIVATED SLUDGE: NORTHSIDE TREATMENT PLANT, DURHAM, NC - EXPERIMENT NO. 2

Compound	Initial Conc. µg/L	Raw Wastewater Influent					Activated Sludge				
		Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r	Log C_w	Log C_s	Slope n	Intercept Log K (K)	Corr. Coef. r
Benzene	1.99	0.272	0.387	1.112	0.04	0.982	-0.020	0.538	0.842	0.60 (3.98)	0.987
	49.8	1.675	1.697				1.387	1.928			
	99.6	1.943	2.378				1.998	2.174			
Chlorobenzene	1.94	0.288	0	0	0	1.0	-0.224	0.454	0.653	0.61 (4.07)	0.996
	48.8	1.688	0				1.533	1.688			
	97.6	1.989	0				1.898	1.791			
Chloroform	1.10	0.040	0	0	0	1.0	-0.120	0.056	0.556	0.07 (1.17)	0.761
	10.9	1.037	0				1.037	0			
	54.4	1.736	0				1.736	1.213			
Toluene	1.99	0.299	0	1.550	-0.44	0.996	0.118	0.353	0.978	0.33 (2.14)	0.968
	49.8	1.697	2.32				1.369	1.944			
	99.6	1.998	2.55				1.998	2.101			

SECTION 6

ESTIMATION OF PURGEABLE PRIORITY POLLUTANT LEVELS IN AIRSTREAMS FROM ACTIVATED SLUDGE

INTRODUCTION

Studies were conducted to determine the levels of purgeable Priority Pollutants in raw wastewater, activated sludge and in the off-gas from activated sludge basins stripped by the aeration process. The objective was to determine the relationship between off-gas concentrations between the front and end of an aeration basin to the concentrations for the same Priority Pollutants in activated sludge collected at the beginning and end of an aeration basin. Furthermore, the significance of the sorption data from Section 5 was to be considered in relating off-gas concentrations to the concentrations of Priority Pollutants in activated sludge. In order to demonstrate this phenomen liquid and air samples were collected simultaneously at several points across an aeration basin.

An additional objective was to delineate the steps necessary to calculate the emission rate for Priority Pollutants as the result of the off-gassing from aeration basins in a wastewater treatment facility. In order to conduct studies to address these two objectives, the Northside Wastewater Treatment plant in Durham, NC which receives a mixture of industrial and municipal raw sewage was selected for this study.

EXPERIMENTAL

Sampling System

The design and fabrication of a Nutech sampler has been previously described (1). The Nutech sampler (Fig. 3) was designed for sampling of "purgeable" organic Priority Pollutants during gas evolution from aeration tanks and grit chambers at wastewater treatment facilities.

The aeration tank may be considered a surface source of nonhomogeneous character where the rate of gas evolution and the concentration of organics

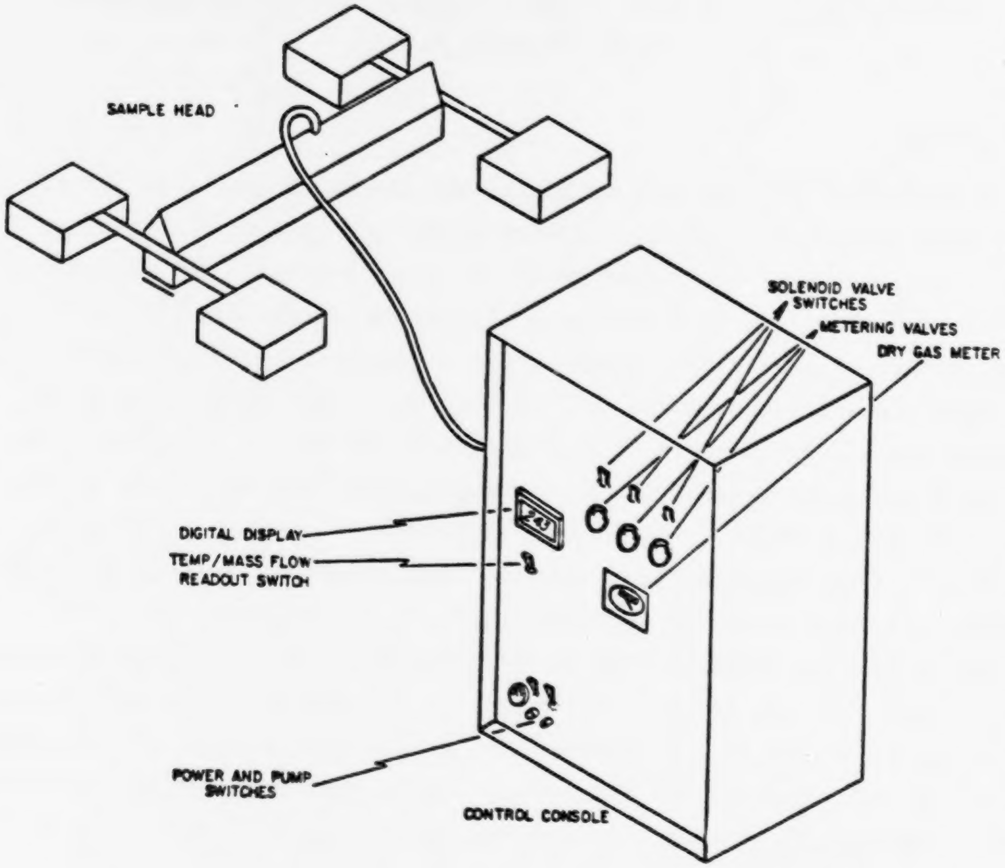

SAMPLE HEAD
SOLENOID VALVE SWITCHES
METERING VALVES
DRY GAS METER
DIGITAL DISPLAY
TEMP/MASS FLOW READOUT SWITCH
POWER AND PUMP SWITCHES
CONTROL CONSOLE

Figure 3. Schematic of sampler system for grit chambers and aeration tanks.

varies from point to point. Time dependence in plug flow and other variabilities may also be expected. Obtaining meaningful data under these conditions requires that the total volume of gas evolving from the surface be determined. The sampling head (Fig. 4) which was designed for this sampler defines a certain surface area and channels all the gases emitted through the appropriate flow monitors. A skirt extends into the liquid (Fig. 4) and defines a source area and provides a low pressure buildup to force the gas through the sampler. For air to liquid (v/v) ratios for typical aeration tanks such as the one at the Northside Treatment plant in Durham, NC, a surface area of 0.365 m^2 should evolve a gas flow within the range of 1 to 30 L/min. The sampling head was designed as a rectangle instead of a square to more representatively capture the off-gas across the tank, thus minimizing variation of emission from center where the diffusors are located to the side of a typical aeration tank.

The initial step in this procedure was selecting an appropriate location for the sampling head and console. The tank design and operation varies considerably from plant to plant. Care was exercised to place the units where sufficient bubble activity was present and where the console and sample head were located within a few feet of each other and within reach of AC power. Three sampling heads and consoles were secured at three locations of aeration tank No. 2 (see Fig. 2) by attaching the support arm to a railing and, for additional stability, attaching ropes to the eyebolts located at the ends of each of the sampling heads.

Typical aeration rates in the tanks were in the range of 26.9 L/min/m^2 of surface area. This rate was determined by passing the total flow through the dry gas meter (Fig. 5) for a short period of time, i.e., about 10 min. During this period the umbilical line and cartridge chamber were stabilized to the operating temperature of 40°C.

Flow through individual cartridge holders (a triplicate set was collected) was set by adjustment of the metering valve (Fig. 5). With the pump switch on, the solenoid valve corresponding to the holder of interest on, and the digital panel meter switch in the mass flow position, the metering valve was slowly opened until the mass flow indication reached the desired level. This procedure was repeated for each of the cartridge holders to establish

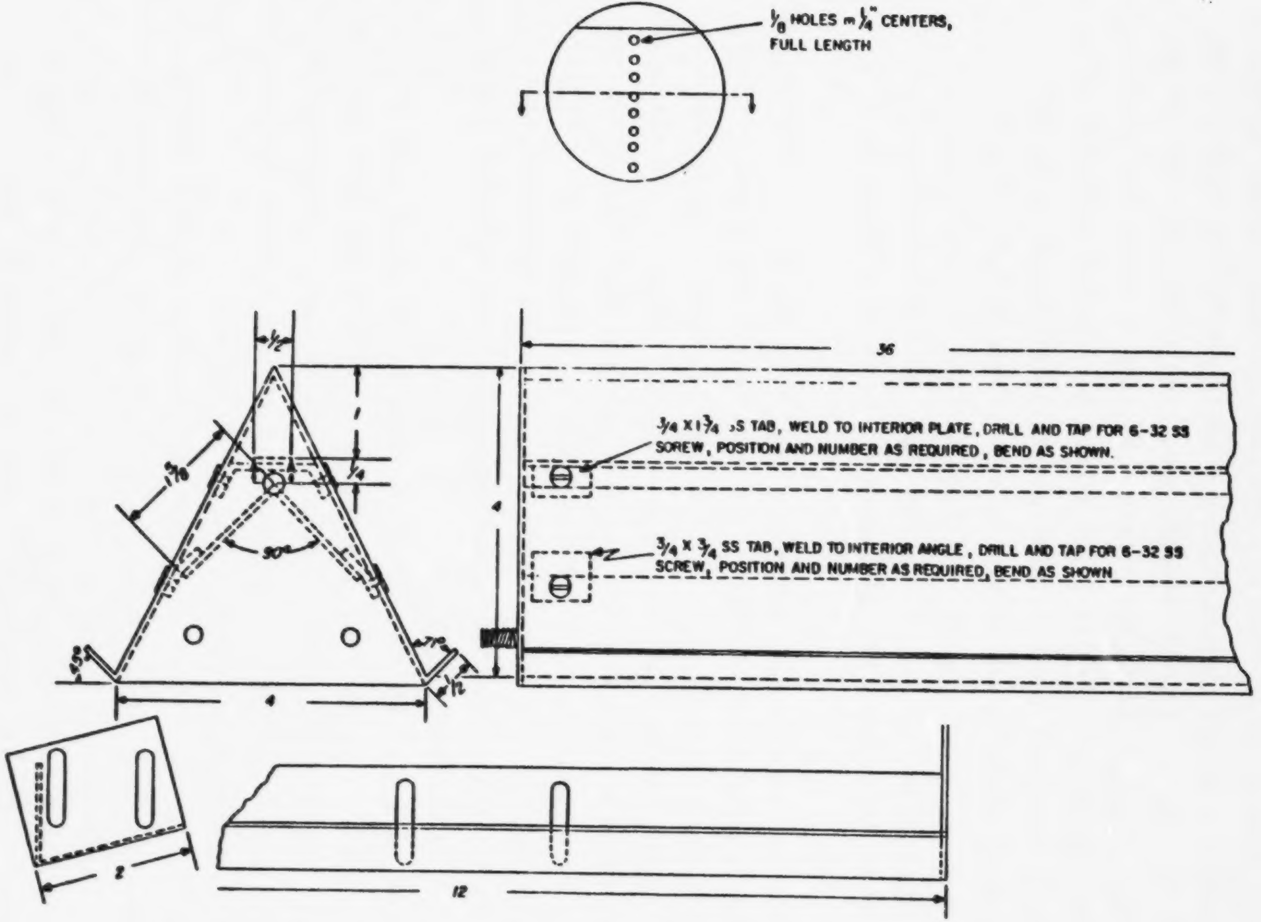

1/8 HOLES ON 1/4" CENTERS, FULL LENGTH
1/2
1
1/4
1 5/16
90°
45°
7/16
1/2
4
4
36
3/4 X 1 3/4 SS TAB, WELD TO INTERIOR PLATE, DRILL AND TAP FOR 6-32 SS SCREW, POSITION AND NUMBER AS REQUIRED, BEND AS SHOWN.
3/4 X 3/4 SS TAB, WELD TO INTERIOR ANGLE, DRILL AND TAP FOR 6-32 SS SCREW, POSITION AND NUMBER AS REQUIRED, BEND AS SHOWN
2
12

Figure 4. Schematic of sampling shroud.

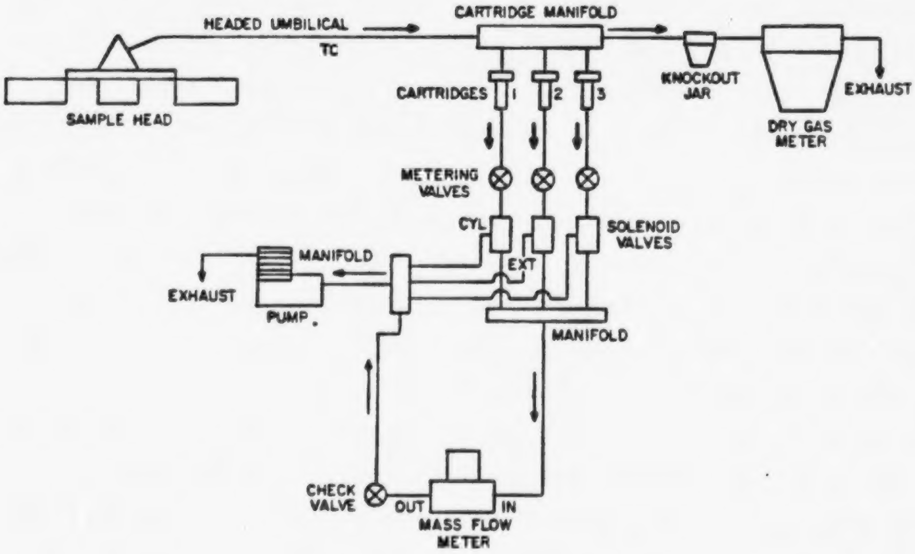

HEADED UMBILICAL
TC
CARTRIDGE MANIFOLD
SAMPLE HEAD
CARTRIDGES
1
2
3
KNOCKOUT JAR
DRY GAS METER
EXHAUST
METERING VALVES
CYL
SOLENOID VALVES
EXT
MANIFOLD
EXHAUST
PUMP
MANIFOLD
CHECK VALVE
OUT
IN
MASS FLOW METER

Figure 5. Diagram of pneumatics in sampler system.

flow through each holder. When the flow rates had been set to the desired level, the solenoid valves were shutoff without disturbing flow settings and the prepared cartridges were installed for sampling (1).

The mass flow control units of the Nutech 851 samplers, capable of triplicate or quadruplicate cartridge sampling, had been calibrated against a bubble flow meter attached to the main pump exhaust. A linear relationship with an intercept of 0 and a slope deviation from unity of <15% was observed for all of the mass flow channels.

Sample Collection/Strategy

Three studies (a pilot and two experiments) were conducted at the Northside Treatment Plant in Durham, NC. Air and liquid samples were collected at two or three locations of the aeration tanks as shown in Figure 2 for each study. Sampling was conducted over a 4.5 h period (approximating hydraulic plug flow) for the Priority Pollutants present in the airstream leaving the activated sludge basin. Samplers were placed at different points along the second aeration basin to determine whether a concentration gradient of Priority Pollutants could be detected in the off-gas between the front and backends of the tank. Simultaneously, liquid samples were collected at the same locations as air, sampling at various time intervals throughout the 4.5 h period.

In the pilot study a triplicate set of air samples was obtained from the second basin at the influent end, and a quadruplicate set near the effluent end (Fig. 2). Grab liquid sludge samples were taken in duplicate from the first, second, fourth, sixth and eighth aeration basins at the beginning and end of the air sampling period (Table 11). Samples were transferred to 60 mL amber bottles sealed with Teflon®-lined caps, stored on ice in the field and then transferred to a cold room at 4°C upon arrival at the laboratory.

In experiments No. 1 and 2 sampling was conducted of the air streams leaving the activated sludge basin at three locations (beginning, middle and end). Two sampling periods were employed covering a total of 4.5 h (Table 12). Triplicate samples of the air stream leaving aeration tank No. 2 were taken at each location during the two time periods (Fig. 2). Concurrently at the beginning, middle and end of the air sampling period, activated

Table 11. SAMPLING PROTOCOL FOR AIR AND SLUDGE SAMPLES: PILOT STUDY - NORTHSIDE TREATMENT PLANT, DURHAM, NC

Aeration Tank No.	Air Samples					Sludge Samples	
	Period	Time	Location	Cartridge	Volume (L)	Period	Time
1	-	-	-	-	-	1	1250
						5	1740
2	1	1300-1730	L1	T1	2.05	1	1305
				T2	2.03		
				T3	1.95	2	1345
	1	1300-1730	L3	T1	2.07	3	1505
				T2	2.02		
				T3	1.98	4	1600
						5	1735
4	-	-	-	-	-	1	1255
						5	1730
6	-	-	-	-	-	1	1300
						5	1725
8	-	-	-	-	-	1	1305
						5	1720

Table 12. SAMPLING PROTOCOLS FOR AIR, ACTIVATED SLUDGE AND RAW WASTEWATER SAMPLES: EXPERIMENTS 1 & 2 - NORTHSIDE TREATMENT PLANT, DURHAM, NC

	Activated Sludge Samples			Air Samples (Aeration Tanks)					Raw Wastewater Samples
Experiment No.[a]	L1	L2	L3	Period No.	Time	Location	Cartridges	Volume (L)	Time
1	1200	1210[b]	1220	1	1200-1415	L1	T1,T2,T3	1.87 ± .07	1305
	1300	1310[b]	1320		1200-1415	L2	T1,T2,T3,T4	1.76 ± .22	1400
	1400	1410[b]	1420		1200-1415	L3	T1,T2,T3,T4	1.81 ± .09	1525
	1500	1510[b]	1520	2	1415-1630	L1	T1,T2,T3	1.94 ± .18	1615
	1600	1610[b]	1620		1415-1630	L2	T1,T2,T3,T4	1.58 ± .20	1740
					1415-1630	L3	T1,T2,T3,T4	1.81 ± .16	
2	1200	1210	1220	1	1200-1415	L1	T1,T2,T3	1.80 ± .08	1130[c]
	1300	1310	1320		1200-1415	L2	T1,T2,T3,T4	1.75 ± .07	
	1400	1410	1420		1200-1415	L3	T1,T2,T3,T4	1.73 ± .09	
	1500	1510	1520	2	1415-1630	L1	T1,T2,T3	1.80 ± .09	
	1600	1610	1620		1415-1630	L2	T1,T2,T3,T4	1.80 ± .13	
					1415-1630	L3	T1,T2,T3,T4	1.75 ± .17	

[a] Experiments No. 1 and 2 were conducted on January 29, and May 14, 1980, respectively. Air and sludge samples were taken at activated sludge aeration tank Nos. 2 and 4 for Expts. No. 1 and 2, respectively.

[b] Not analyzed for "purgeable" Priority Pollutants.

[c] Collected only for sorption studies.

sludge samples were taken from the same locations in this tank (Fig. 2). Table 12 gives the sampling parameters for both experiments.

In the second experiment raw wastewater and samples of ambient air leaving aeration tank No. 2 were taken over a 4.5 h period. Again three flotation heads of 0.365 m^2 dimensions were placed at the initial, middle and final sites of plug flow in aeration tank No. 2 (see Fig. 2). The mass flow controllers were set at 13 mL/min via previously established mass flow/exhaust flow calibration curves. Triplicate samples were adsorbed onto 1.5 cm x 6.0 cm Tenax cartridges for 2 h and 15 min each. The cartridges were then replaced with a second set and sampling continued for the remaining period of time (see Table 12). Activated sludge samples from three locations along aeration tank No. 2 were also taken in duplicate approximately every hour.

Volatile Organic Analysis (Sludge and Wastewater)

The purging method as described in the EPA Protocol for Sludge was utilized (6). Pooling of three aqueous samples gave an average dry solid sludge concentration of 3 mg/mL. Although such a solid concentration would be well below an established EPA Protocol gradient (50 mg/10 mL for an undiluted sample) an arbitrary dilution of 1:10 with distilled water was employed to avoid possible saturation during GC/MS analysis.

The diluted suspensions were purged with helium at 40 mL/min for 12 min onto a 1.5 cm x 6.0 cm 30/60 mesh Tenax cartridge as previously described (6). Samples were stored over activated calcium sulfate with the addition of external standards (perfluorotoluene and perfluorobenzene) and then submitted to GC/MS for analysis.

Air Samples

Tenax cartridges were stored over activated calcium sulfate overnight. Internal standards of perfluorobenzene and perfluorotoluene (~400 ng) were loaded on each cartridge and samples were analyzed by GC/MS. The procedures employed were as previously described (1).

Quality Control and Quality Assurance

Reagents, Solvents and Glassware--

All solvents employed were obtained from Burdick and Jackson (Muskegan, MI) and were redistilled prior to use. Chemicals used as standard reference materials were analytical reagent grade. Glassware was washed in non-detergent soap, rinsed with deionized water, dried and then heated to 450°C in an oven for 2 h.

Air Samples--

Unexposed Tenax GC cartridges served as blanks from each batch prepared for air sampling. The compounds listed in Table 13 were loaded onto Tenax cartridges and served as controls for instrument calibration (1). Twenty-three Priority Pollutants were loaded onto standard cartridges via a flash tube evaporation system at 247°C as monitored by a thermocouple readout. Samples were loaded via a 2 μL methanol injection into cryogenically scrubbed helium at a flow of 50 mL/min for 24 min. These cartridges served as standards for the ambient air sample analysis. Blanks and controls were analyzed along with samples.

Purgeable Organics from Liquid Samples--

Deionized-distilled water (prepurged) was spiked with the Priority Pollutants listed in Table 13. The same compounds were added to 960 mL of purged distilled water using methanol as the solvent. A minimum of 2 h was allowed for equilibration. These samples were then employed as a source of purge controls and no aliquot was employed 5 h after the preparation of this solution. Unexposed Tenax cartridges served as blanks. Blanks and controls were analyzed along with samples. Recoveries for water controls are given in Table 13.

Instrumental Analysis

Priority Pollutants purged from liquid samples and cartridges used to collect Priority Pollutants from the airstream were analyzed according to previously described methods (1).

RESULTS AND DISCUSSION

The Priority Pollutant levels in the airstreams from an aeration tank at the Northside Treatment Plant in Durham, NC are given in Table 14. Also the levels for the same Priority Pollutants measured in the activated sludge from aeration tank No. 2 are provided. Comparison of the air levels of Priority Pollutants at locations 1 and 3 (representing the entrance and exit of liquid flow for the aeration tank) indicates lower levels of Priority Pollutants at the exit. For the most part, a decrease by a factor of 2 to 3

Table 13. RECOVERY OF PRIORITY POLLUTANTS USED IN QUALITY CONTROL

Compound	Quantity added to air sampling cartridges (ng)	Quantity added to 10 ml "purged" waters (ng)	% Recovery		
			Control No. 1	Control No. 2	Control No. 3
bis(2-chloroethyl)ether	244	254	ND[a]	ND	-
1,1,1-trichloroethane	268	279	78	87	107 ± 3
1,2-dichloropropane	231	241	83 ± 8	99	75 ± 12
toluene	260	270	82 ± 14	86	68 ± 7
ethylbenzene	260	270	56 ± 1	-	-
1,1-dichloroethane	235	245	-	-	100 ± 1
bromodichloroethane	297	308	82 ± 1	116	67 ± 12
bromoform	289	300	42 ± 2	-	-
chlorobenzene	221	345	58 ± 14	76	-
chloroform	224	310	85 ± 1	115	83 ± 6
ethylene dichloride	251	262	85 ± 22	-	-
tetrachloroethylene	243	337	35 ± 4	69	-
1,1,2,2-tetrachloroethane	238	327	82 ± 14	-	-
1,3-dichlorobenzene	258	268	51	72	-
acrylonitrile	242	252	ND	ND	-
trichloroethylene	219	304	59	102	55 ± 7
carbon tetrachloride	239	331	65	65	49 ± 3
benzene	262	272	73 ± 6	-	65 ± 4
trans-1,2-dichloroethylene	251	262	111 ± 4	-	84 ± 3
methylene chloride	265	275	-	-	-
1,1,2-trichloroethane	287	300	39 ± 2	-	-
1,2-dichlorobenzene	261	270	57 ± 4	-	-
acrolein	252	265	-	-	-

[a] ND = not detected, - = not measured, values where indicated are mean ± S.D. for triplicate determinations, background subtract for "blanks".

Table 14. PRIORITY POLLUTANT LEVELS IN AIRSTREAMS AND ACTIVATED SLUDGE FROM AERATION TANK NO. 2: PILOT STUDY - NORTHSIDE TREATMENT PLANT, DURHAM, NC (August 19, 1979)

Priority Pollutant	Air[a]		Sludge[b]
	L1	L3	
Methylene chloride	53.1 ± 8.5	37.7 ± 4.3	32.4 ± 12.4
Trichlorofluoromethane	21.4 ± 4.8	6.3 ± 0.6	3.6 ± 1.8
1,1-Dichloroethylene	3.4 ± 1.4	5.4 ± 0.3	T
Chloroform	521.4 ± 172.6	129.7 ± 28.9	1.2 ± 1.2
1,1,1-Trichloroethane	25.5 ± 3.3	5.4 ± 1.3	2.1 ± 0.6
Carbon tetrachloride	ND	ND	ND
Bromodichloromethane	15 ± 3.4	8.4 ± 1.6	ND
Trichloroethylene	49.6 ± 5.9	22.8 ± 5.0	5.8 ± 1.4
Benzene	87.6 ± 28.5	24.8 ± 0.6	7.6 ± 1.7
Tetrachloroethylene	463.2 ± 27.9	109.3 ± 8.8	2.5 ± 0.1
1,1,2,2-Tetrachloroethane	T	ND	T
Toluene	680.3 ± 3.9	24.2 ± 1.0	13.6 ± 2.0
Chlorobenzene	8.9 ± 1.5	3.4 ± 1.3	0.7 ± 0.7
Ethylbenzene	94.3 ± 7.9	15.7 ± 5.4	1.2 ± 0.4
Dichlorobenzene isomer	287.1 ± 12.9	133.1 ± 12.1	5.6 ± 1.5

[a] Mean values are in ppb with standard deviation for triplicate samples.

[b] Average values are in ppb with variation for duplicate samples.
T = trace, ND = not detected.

was observed. The concentration in the activated sludge at the entrance of aeration tank No. 2 is also indicated in Table 14. The concentrations of the Priority Pollutants in the off-gas represent an integration over a period of 4.5 h while the average concentration in the sludge is for a grab sample at the beginning and end of each sampling period. In this Pilot Study no inference can be drawn regarding the relationship between the concentrations of the Priority Pollutants in sludge and in the off-gas from the aeration basin.

Table 15 provides a comparison of the Priority Pollutant levels in activated sludge at two different time periods in five aeration tanks. The mean value, standard deviation and coefficient of variation were calculated for each of the Priority Pollutants that were in measurable quantities. Examination of the coefficients of variation indicates that a considerable variation occurs between the aeration tanks despite the fact that samples were collected at the same location, i.e., at the flow entrance into each aeration tank. This variation suggests that obtaining precise measurements of Priority Pollutant concentrations is difficult in activated sludge. Whether this problem resides with the analytical methodology or is reflective of the large variations in the input levels from one aeration tank to another is unknown. Nevertheless, the Priority Pollutant levels in activated sludge varied as much as 60% between the beginning and end of sampling of off-gas from the aeration tank.

Table 16 presents the Priority Pollutant levels in raw wastewater in the first experiment performed at the Northside Treatment Plant in Durham, NC. The Priority Pollutants were determined at several different times during a concurrent sampling of the off-gas from the aeration tanks. Fourteen of the 34 volatile Priority Pollutants were detected in the raw wastewater samples. Examination of the raw wastewater samples taken at various times indicated that the Priority Pollutant levels varied up to a factor of 3 over the 4.5 h period of the experiment.

Table 17 presents the Priority Pollutant levels in airstreams and activated sludge from aeration tank No. 2 also for experiment No. 1. Results for air levels are presented for two different time intervals and three locations (entrance, middle, exit) and for levels in sludge at the beginning

Table 15. COMPARISON OF PRIORITY POLLUTANT LEVELS IN ACTIVATED SLUDGE AT TWO DIFFERENT TIME PERIODS: NORTHSIDE TREATMENT PLANT, DURHAM, NC - PILOT STUDY

Priority Pollutant	T = 0 h					T = 4 h					Mean ± S.D. (C.V.)
	AT1[a]	AT2	AT4	AT6	AT8	AT1	AT2	AT4	AT6	AT8	
Methylene chloride	21.8[b]	44.7	11.7	21.4	30.3	44.6	20.0	46.8	46.4	35.6	32.3 ± 13 (40)
Trichlorofluoromethane	1.7	5.5	1.8	1.3	1.7	6.2	1.8	3.0	3.0	3.0	2.9 ± 1.7 (58)
1,1-Dichloroethylene	T[c]	T	ND[d]	ND	ND	ND	ND	ND	ND	ND	T
Chloroform	2.0	2.3	2.4	1.9	1.8	3.4	ND	3.7	3.5	2.4	2.3 ± 1.1 (47)
1,1,1-Trichloroethane	1.1	1.5	0.9	ND	0.8	2.8	2.7	2.7	2.4	3.7	1.9 ± 1.2 (61)
Carbon tetrachloride	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromodichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	5.1	7.2	5.2	-	4.3	5.7	4.5	4.5	2.4	4.5	4.3 ± 1.9 (45)
Benzene	7.3	9.3	7.1	-	7.0	8.7	5.9	9.2	8.2	10.5	7.3 ± 2.9 (40)
Tetrachloroethylene	2.0	2.6	1.7	1.3	1.3	2.9	2.5	2.9	2.0	2.0	2.1 ± 0.6 (28)
1,1,2,2-Tetrachloroethane	ND	T	ND	ND	ND	ND	ND	ND	ND	ND	T
Toluene	12.7	15.6	8.9	7.3	15.5	12.6	11.6	2.6	1.6	1.6	9.0 ± 5.5 (61)
Chlorobenzene	2.1	1.4	ND	1.3	1.2	1.7	T	1.3	1.3	1.3	1.3 ± 0.5 (41)
Ethylbenzene	1.3	1.6	ND	1.0	1.4	1.3	0.8	T	1.3	T	1.1 ± 0.5 (40)
Dichlorobenzene	5.5	4.1	5.9	3.9	4.1	7.5	7.1	7.1	5.7	7.1	5.8 ± 1.4 (24)

[a] AT1 = aeration tank, No. 1, etc., see Fig. 2 , samples taken at entrance.

[b] Values are in ppb.

[c] T = trace.

[d] ND = not detected.

Table 16. PRIORITY POLLUTANT LEVELS IN RAW WASTEWATER: NORTHSIDE TREATMENT PLANT, DURHAM, NC - EXPERIMENT NO. 1 (JANUARY 29, 1980)

	Sampling Time (h)				
Priority Pollutant	1305	1400	1525	1615	1740
Chloromethane	T[a]	0.8 ± 0.05	0.7 ± 0.30	T	T
Dichlorodifluoromethane	ND	ND	ND	ND	ND
Bromomethane	ND	ND	ND	ND	ND
Vinyl chloride	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND
Methylene chloride	NC	NC	NC	NC	NC
Trichlorofluoromethane	ND	ND	ND	ND	ND
1,1-Dichloroethylene	ND	ND	ND	ND	ND
1,1-Dichloroethane	T	ND	ND	ND	T
trans-1,2-Dichloroethylene	ND	ND	ND	ND	ND
Chloroform	8.5 ± 1.10	6.1 ± 1.40	6.8 ± 0.5	7.2	10.8
1,2-Dichloroethane	T	2.5 ± 1.00	ND	5.8 ± 1.00	ND
1,1,1-Trichloroethane	1.8 ± 0.30	1.5 ± 0	2.0 ± 0.70	1.6	9.1
Carbon tetrachloride	ND	T	ND	T	T
Bromodichloromethane	T	ND	ND	ND	ND
Bis(2-chloroethyl)ether	ND	ND	ND	ND	ND
1,2-Dichloropropane	ND	ND	ND	ND	ND
trans-1,2-Dichloropropene	ND	ND	ND	ND	ND
Trichloroethylene	0.6 ± 0.10	0.4 ± 0.20	0.4 ± 0.05	0.5 ± 0	0.7 ± 0

(continued)

Table 16 (cont'd.)

Priority Pollutant	Sampling Time (h)				
	1305	1400	1525	1615	1740
Dibromochloromethane	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	ND	ND	ND
Benzene	2.2 ± 0.20	2.5 ± 0.50	2.4 ± 0.10	3.0 ± 0.60	3.8
2-Chloroethyl vinyl ether	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethylene	5.1 ± 0.60	2.6 ± 0.40	3.5 ± 0.40	5.5 ± 0.70	4.7
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND
Toluene	11.7 ± 1.50	6.7 ± 2.30	8.8 ± 0.50	20.1 ± 3.90	26.2
Chlorobenzene	ND	T	ND	ND	ND
Ethylbenzene	1.7 ± 0.50	0.9 ± 0.20	0.8 ± 0.10	1.7 ± 0.10	2.1 ± 0.60
Acrolein	ND	8.9 ± 0.40	6.5 ± 0.70	T	T
Acrylonitrile	T	ND	ND	ND	T
o-Dichlorobenzene	0.8 ± 0.20	0.5 ± 0.05	0.5 ± 0.05	0.5 ± 0	0.8 ± 0.10
m-Dichlorobenzene	2.2 ± 0.10	1.8 ± 0.30	2.3 ± 0.05	1.6 ± 0	2.5 ± 0.30

[a] T = trace, ND = not detected, NC = not calculated. Values are in ppb.

Table 17. PRIORITY POLLUTANT LEVELS IN AIRSTREAMS AND ACTIVATED SLUDGE FROM AERATION TANK NO. 2: NORTHSIDE TREATMENT PLANT, DURHAM, NC - EXPERIMENT NO. 1 (JANUARY 29, 1980)

	L1				L2		L3			
	1200-1415 h		1415-1630 h		1222-1435 h	1440-1650 h	1240-1455 h		1455-1705 h	
Priority Pollutant	Air	Sludge[a]	Air	Sludge[b]	Air	Air	Air	Sludge[a]	Air	Sludge[b]
Chloromethane	ND[c]	0.4 (0.02)	ND	0.5 (0.05)	ND	ND	ND	0.3 (0)	ND	0.7 (0.02)
Dichlorodifluoromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Vinyl chloride	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methylene chloride	14.6 (4.9)	NC	T	NC	34.6 (13)	T	38.9 (8.3)	NC	40.9 (4.3)	NC
1,1-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	2.3 (5.4)	ND	1.5 (2.7)	ND	1.5 (2.4)	T	ND	0.1 (0)	ND	T
trans-1,2-Dichloroethylene	1.4 (2.7)	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	54.9 (6.1)	1.3 (0.3)	30.6 (1.2)	2.3 (0.4)	42.9 (10)	56.7 (6.5)	23.9 (9.2)	3.1 (1.00)	30.4 (1.6)	3.7 (1.10)
1,2-Dichloroethane	1.5 (8.1)	ND	T	ND	2.2 (6.6)	T	ND	T	ND	T
1,1,1-Trichloroethane	17.8 (3.3)	0.9 (0.01)	8.4 (1.6)	1.9 (0.10)	11.8 (8.7)	12.7 (0.8)	3.5 (8.5)	1.3 (0.17)	3.8 (2.5)	1.3 (0.08)
Carbon tetrachloride	T	0.2 (0.02)	T	1.4 (0.02)	T	T	T	ND	T	ND
Bromodichloromethane	2.4 (0.7)	ND	7.9 (0.9)	ND	8.1 (0.4)	8.0 (3.7)	T	ND	5.4 (2.6)	ND
Bis(2-chloroethyl)ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
trans-1,2-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	9.1 (1.9)	0.2 (0.02)	5.7 (4.0)	T	5.7 (4.0)	4.7 (0.5)	2.2 (4.5)	T	2.9 (2.1)	T
Dibromochloromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	T	ND	ND	ND	ND	ND	ND	ND
Benzene	14 (6)	3.5 (0.80)	3.3 (7)	3.2 (0.60)	3.8 (6)	3.9 (9.7)	2.2 (15)	1.9 (0.30)	2.4 (6)	1.5 (0.02)

(continued)

Table 17 (cont'd.)

	L1				L2		L3			
	1200-1415 h		1415-1630 h		1222-1435 h	1440-1650 h	1240-1455 h		1455-1705 h	
Priority Pollutant	Air	Sludge[a]	Air	Sludge[b]	Air	Air	Air	Sludge[a]	Air	Sludge[b]
2-Chlorovinyl vinyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethylene	72.3 (2.7)	1.1 (0.10)	26.4 (3.0)	1.5 (0.43)	25.1 (2.4)	62.8 (5.4)	16.4 (2.3)	0.4 (0.05)	20.9 (3.0)	0.8 (0.20)
1,1,2,2-Tetrachloroethane	ND	ND	3.0 (4.2)	ND	T	ND	T	ND	T	ND
Toluene	95.3 (5.0)	11.3 (1.60)	5.5 (5.50)	9.4 (0.10)	5.8 (4.50)	4.3 (0.1)	4.5 (4.5)	9.1 (0.80)	T	10.8 (1.47)
Chlorobenzene	ND	ND	T	ND	T	1.6 (0.4)	ND	ND	ND	ND
Ethylbenzene	ND	0.4 (0.05)	1.8 (6.1)	0.4 (0.02)	1.6 (7.04)	2.9 (5.9)	ND	0.4 (0.02)	ND	0.3 (0.03)
Acrolein	ND	10.2 (1.6)	ND	4.6 (0.02)	ND	ND	ND	8.0 (1.35)	ND	7.1 (1.50)
Acrylonitrile	ND	ND	ND	ND	ND	ND	ND	2.3 (0.35)	ND	1.0 (0.10)
o-Dichlorobenzene	9.0 (0.3)	0.3 (0.03)	7.7 (2.6)	0.4 (0.05)	7.4 (2.9)	7.9 (5.5)	3.9 (3.9)	0.2 (0.0)	4.0 (0.6)	0.1 (0.0)
m-Dichlorobenzene	30.5 (0.6)	0.6 (0.06)	27.6	0.8 (0.20)	26.6 (1.0)	39.0 (6.0)	18.9 (1.5)	0.8 (0.01)	21.3 (0.8)	0.8 (0.08)

[a] Priority Pollutants were measured in sludge at the beginning and end of time period.

[b] Priority Pollutants were measured at the beginning, middle and end of time period.

[c] ND = not detected, T = trace, mean values are in ppb with coefficient of variation in parenthesis.

and end of each air sampling period at two locations in the sludge. In general, a decrease in the Priority Pollutant levels was observed in the airstreams between locations 1, 2 and 3, respectively. However, the Priority Pollutant levels in the activated sludge at locations 1 and 3 in the tank for either of the sampling periods do not decrease. The reason for the absence of a gradient in sludge between the front and end of the tank is not clearly understood. Since it is possible that the Priority Pollutants are distributed between the solid and liquid phases (as shown by the sorption data in Table 7) the concentration which is measured for the liquid sample appears to be relatively constant. This observation may be misleading. A plausible explanation may be that the Bellar and Lichtenberg method (a He stripping method) for measuring "purgeable" Priority Pollutants in sludge is more efficient in removing organics dissolved in water (liquid phase) and adsorbed to solids than the areation process in an activated sludge tank. Thus, the sorption of organics to solids is reversed and they are stripped from the liquid medium.

Comparison of the Priority Pollutant levels in raw wastewater with activated sludge reveals significantly higher levels are generally found in the raw sewage. Thus, vaporization of Priority Pollutants to the atmosphere probably has occurred in other parts of the treatment facility (e.g., at roughing filters, vacuators, etc.) prior to reaching the aeration basins.

A second experiment was conducted at the Northside Treatment Plant in Durham, NC. Again Priority Pollutant levels were measured in airstreams and activated sludge. In this case the experiment was performed at aeration tank No. 4 on May 14, 1980. These results are given in Table 18. A comparison of the levels of the Priority Pollutants for this experiment with the the pilot study and experiment No. 1 indicates a considerable variation in the Priority Pollutant levels in the off-gas from aeration tanks. Also considerable differences are observed for concentrations in the activated sludge.

The results in experiment No. 2 (Table 18) also show a decreasing level of Priority Pollutants in the off-gas between the flow entrance (L1) and exit (L3) through the aeration tank. Again, as in experiment No. 2 (Table

Table 18. PRIORITY POLLUTANT LEVELS IN AIRSTREAMS AND ACTIVATED SLUDGE FROM AERATION TANK NO. 4: NORTHSIDE TREATMENT PLANT, DURHAM, NC - EXPERIMENT NO. 2 (MAY 14, 1980)

Priority Pollutant	L1				L2				L3			
	1200-1415 h		1415-1630 h		1215-1430 h		1430-1645 h		1215-1430 h		1430-1650	
	Air	Sludge[a]	Air	Sludge	Air	Sludge	Air	Sludge	Air	Sludge	Air	Sludge
Chloromethane	ND[b]	ND	ND	ND	ND	ND	ND	T	ND	ND	ND	ND
Dichlorofluoromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bromoethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Vinyl chloride	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methylene chloride	27.7±6.3	18.5±7.8	23.7±2.0	34.2±21.6	9.7±1.0	51.4±6.0	7.1±0.6	27.9±3.2	12.3±3.7	79.5±29.0	17.1±0.3	72.9±23.6
Trichlorofluoromethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1-Dichloroethylene	8.0±0.2	4.0±0.4	6.8±0.2	3.9±0.8	T	2.8	ND	ND	ND	ND	ND	ND
1,1-Dichloroethane	2.8±0.5	ND	3.8±0.5	ND	T	ND	T	ND	3.7±1.1	2.3±2.3	ND	ND
trans-1,2-Dichloroethylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chloroform	125±47.7	27.8±13.2	108±13.8	16.7±5.8	52.9±13.9	10.9±1.0	26.5±2.9	16.5±1.4	T	11.2±11.2	8.4±0.6	ND
1,2-Dichloroethane	1.1±0.1	ND	T	0.2±0	T	ND	ND	ND	ND	ND	T	ND
1,1,1-Trichloroethane	27.6±7.4	1.4±0.3	34.0±4.4	1.2±0.1	6.7±1.4	1.1±0.6	6.4±0.7	1.9±0.3	T	0.4±0	1.3±0.2	0.4±0.3
Carbon tetrachloride	ND	0.2±0	T	0.3±0.1	T	T	ND	ND	ND	ND	T	ND
Bromodichloromethane	4.7±0.8	ND	3.4±0.1	ND	T	ND	2.1±0.1	ND	ND	ND	ND	ND
Bis(2-chloroethyl)ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
trans-1,2-Dichloropropene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trichloroethylene	10.7±0.4	0.4±0	9.4±2.8	0.6±0.1	3.1±0.6	0.4±0.1	1.7±0.2	0.4±0.1	4.4	0.4±0.1	4.8±1.7	0.3±0
Dibromochloromethane	ND	ND	T	ND	T	ND	ND	ND	ND	ND	ND	ND
cis-1,3-Dichloropropane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2-Trichloroethane	ND	ND	T	ND	ND	ND	ND	ND	ND	ND	ND	ND

(continued)

Table 18 (cont'd.)

	L1				L2				L3			
	1200-1415 h		1415-1630 h		1215-1430 h		1430-1645 h		1215-1430 h		1430-1650	
Priority Pollutant	Air	Sludge[a]	Air	Sludge	Air	Sludge	Air	Sludge	Air	Sludge	Air	Sludge
Benzene	21.2±4.2	1.0±0.2	18.8±1.5	1.1±0.1	4.8±0.9	1.3±0.2	2.7±0.3	1.1±0.2	7.2	1.2±0.3	7.9±2.7	0.9±0.3
2-Chloroethyl vinyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethylene	119±26.3	4.3±0.7	281±20.4	12.2±2.1	32.1±9.8	2.8±0.4	40.9±4.4	3.8±0.8	3.1±0.1	1.7±0.5	6.0±1.1	1.3±0.2
Bromoform	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,1,2,2-Tetrachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Toluene	136±52.4	3.1±1.1	130±15	3.5±1.0	18.4±6.0	21.4±20.0	5.5±1.0	1.9±0.3	27.1±5.5	10.9±9.3	8.1±0	11.6±8.6
Chlorobenzene	T	ND	T	ND	ND	ND	ND	ND	ND	T	ND	T
Ethylbenzene	26.4±8.4	0.7±0.2	23.4±6.6	0.4±0.4	9.1±1.4	0.5±0.1	4.3±0.5	0.4±0.1	0.9±0	0.3±0.1	0.7±0.3	0.1±0.1
Acrolein	ND	ND	ND	ND	ND	ND	ND	1.7±1.7	ND	ND	ND	ND
Acrylonitrile	ND	ND	T	ND	ND	ND	ND	ND	ND	ND	ND	ND
m-Dichlorobenzene	38.1±13.2	3.6±0.4	36.3±6.9	3.9±1.2	31.6±7.4	3.0±1.4	14.0±1.6	3.6±1.4	4.2±0.2	3.0±1.1	4.3±0.6	2.9±0.4
o-Dichlorobenzene	11.3±2.4	2.5±0.6	10.5±2.6	2.5±0.8	10.2±2.7	1.8±0.4	3.9±0.6	2.1±0.5	1.1±0	1.6±0.1	1.3±0.2	1.7±0.4

[a] Priority Pollutants were measured in sludge at the beginning and end of time period with the mean value of quadruplicate analyses reported.

[b] ND = not detected, T = trace, mean values are in ppb with standard deviation.

17), the concentrations of the Priority Pollutants in sludge were relatively constant or slightly increased in some cases at each of the locations.

In order to estimate the emission rates from the entire composite aeration tank area, it is necessary to have the following pieces of data: (1) the off-gas volume flow per square foot of tank area; (2) the total number of square feet for the composite tank area; and (3) the concentration of the Priority Pollutant in the off-gas per unit time. The off-gas flow rate per unit area can be obtained by one of two methods. The off-gas volume may be obtained from the air injection rate recorded by the plant (gas flow pumped through the diffusers in the aeration tanks). A second method is to determine the off-gas flow rate per unit area with the Nutech sampler. Since the total off-gas flow per square foot passes through and is recorded by the gas meter on the sampler, it is thus possible to obtain a total flow per unit time or period of sampling. An average off-gas rate can be calculated.

Emission rates were calculated for selected Priority Pollutants and for each study (Pilot and Expts. No. 1 and 2) to determine the extent of pollution associated with the aeration tanks at the Northside Treatment Plant in Durham. An example calculation for chloroform (Pilot Study) is as follows:

(1) off-gas rate - 26.90 $\mathrm{L/min/m^2}$

(2) total surface area of aeration tanks -

$$\frac{4.571\ \mathrm{m} \times 61.0\ \mathrm{m}}{\mathrm{tank}} \times 8\ \mathrm{tanks} = 2230.6\ \mathrm{m}^2$$

(NOTE: only 8 of 9 tanks were operating)

(3) total off-gas volume/h -

$$\frac{26.9\ \mathrm{L}}{\mathrm{min} \cdot \mathrm{m}^2} \times 2230.6\ \mathrm{m}^2 \times \frac{60\ \mathrm{min}}{\mathrm{h}} \times \frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}} = 3{,}600\ \frac{\mathrm{m}^3}{\mathrm{h}}$$

(4) mean chloroform level per tank -

$$325\ \mathrm{ppb} \times 4.92\ \frac{\mu\mathrm{g}}{\mathrm{L}} \times \frac{1000\ \mathrm{L}}{\mathrm{m}^3} \times \frac{1\ \mathrm{g}}{10^6\ \mu\mathrm{g}} = \frac{1.599\ \mathrm{g}}{\mathrm{m}^3}$$

where 1 ppb = 4.92 $\frac{\mu\mathrm{g}}{\mathrm{L}}$

(5) emission rate -

$$\frac{1.599\ g}{m^3} \times \frac{3,600\ m^3}{h} = 5,756.4\ g/h$$

Emission rates for all of the studies for each Priority Pollutant measured are given in Table 19. The highest rates were observed for chloroform and 1,1,2,2-tetrachloroethylene with emissions reaching 5.7 kg/h and 7.0 kg/h, respectively, in the Pilot Study.

Table 19. ESTIMATED EMISSION RATES CALCULATED FOR SELECTED PRIORITY POLLUTANTS FROM AERATION BASINS AT NORTHSIDE TREATMENT PLANT, DURHAM, NC

Priority Pollutant	Emission Rates (g/h)		
	August 19, 1979	January 29, 1980	May 14, 1980
Methylene chloride	572	280 ± 86	205 ± 3
1,1-Dichloroethane	-	14 ± 4	19 ± 2
Chloroform	5,756	703 ± 11	944 ± 103
1,2-Dichloroethane	-	10 ± 7	5 ± 2
1,1,1-Trichloroethane	301	191 ± 27	252 ± 23
Bromodichloromethane	288	130 ± 42	43 ± 1
Trichloroethylene	704	103 ± 11	111 ± 8
Benzene	668	62 ± 9	122 ± 8
1,1,2,2-Tetrachloroethylene	7,007	940 ± 15	1,969 ± 710
Toluene	4,819	264 ± 216	741 ± 86
Ethylbenzene	871	16 ± 8	171 ± 21
o-Dichlorobenzene	4,689	148 ± 3	478 ± 71
m-Dichlorobenzene		609 ± 44	155 ± 13

SECTION 7

IDENTIFICATION OF CHLORINATED COMPOUNDS IN SLUDGE FROM A SUPERCHLORINATION PROCESS

INTRODUCTION

Sampling and analysis for chlorinated compounds which might be produced by the stabilization of sludge via a superchlorination process were conducted. The objective of this study was to determine whether any chlorinated organics were present in the fraction which is amenable to gas chromatography since reports indicate 1 to 3% chlorine was associated with the organics (3,4). Sampling and analysis was conducted for qualitative characterization of chlorinated organics using electron impact and negative ion chemical ionization capillary gas chromatography/mass spectrometry (GC/NICIMS).

EXPERIMENTAL

Plant Characteristics

Two plants were sampled. The first was located in Rocky Mount, NC. The sewage treatment plant of Rocky Mount operates with an average flow of 0.5 m^3/sec (~50% industrial) and an average chlorination dose of 800 to 900 mg chlorine per liter of sludge influent, and an average time of 24 h in settling beds. Figure 6 depicts a schematic of the superchlorination process and the locations where samples were obtained. The second plant was located in Fayetteville, NC, and operated under similar conditions.

Sampling

Grab samples of digested influent and chlorinated effluent were taken in duplicate at three 1 h intervals from access valves (Fig. 6). A glass funnel washed after each sample duplicate was used to direct the pressurized flow into 1 L amber bottles which were sealed with Teflon®-lined caps. Semisolid samples from the settling beds (Fig. 7 and 8) were scooped with a 1 L beaker and transferred via a glass funnel to 1 L glass amber bottles with Teflon®-lined caps. Cake sludge from the settling beds was transferred

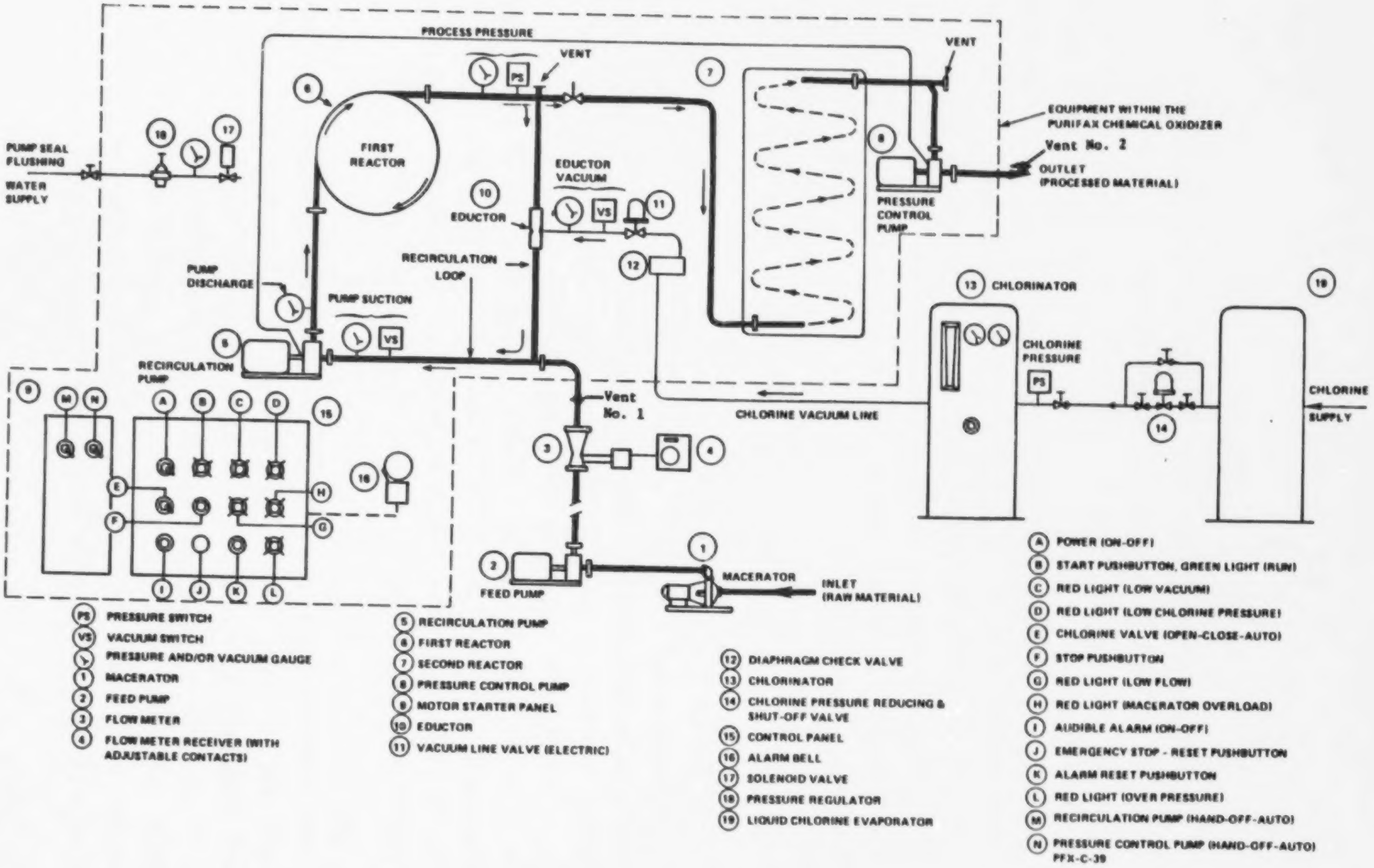
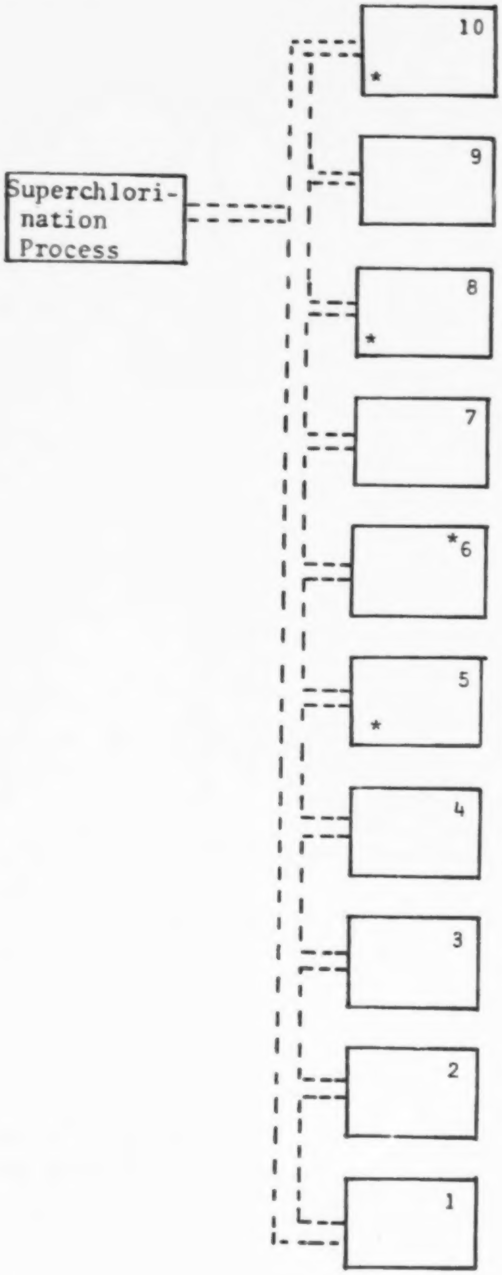

PROCESS PRESSURE
VENT
VENT
FIRST REACTOR
EQUIPMENT WITHIN THE PURIFAX CHEMICAL OXIDIZER
Vent No. 2
OUTLET (PROCESSED MATERIAL)
PUMP SEAL FLUSHING
WATER SUPPLY
EDUCTOR VACUUM
EDUCTOR
PRESSURE CONTROL PUMP
RECIRCULATION LOOP
PUMP DISCHARGE
PUMP SUCTION
CHLORINATOR
CHLORINE PRESSURE
RECIRCULATION PUMP
Vent No. 1
CHLORINE VACUUM LINE
CHLORINE SUPPLY
FEED PUMP
MACERATOR
INLET (RAW MATERIAL)
PS PRESSURE SWITCH
VS VACUUM SWITCH
PRESSURE AND/OR VACUUM GAUGE
1 MACERATOR
2 FEED PUMP
3 FLOW METER
4 FLOW METER RECEIVER (WITH ADJUSTABLE CONTACTS)
5 RECIRCULATION PUMP
6 FIRST REACTOR
7 SECOND REACTOR
8 PRESSURE CONTROL PUMP
9 MOTOR STARTER PANEL
10 EDUCTOR
11 VACUUM LINE VALVE (ELECTRIC)
12 DIAPHRAGM CHECK VALVE
13 CHLORINATOR
14 CHLORINE PRESSURE REDUCING & SHUT-OFF VALVE
15 CONTROL PANEL
16 ALARM BELL
17 SOLENOID VALVE
18 PRESSURE REGULATOR
19 LIQUID CHLORINE EVAPORATOR
A POWER (ON-OFF)
B START PUSHBUTTON, GREEN LIGHT (RUN)
C RED LIGHT (LOW VACUUM)
D RED LIGHT (LOW CHLORINE PRESSURE)
E CHLORINE VALVE (OPEN-CLOSE-AUTO)
F STOP PUSHBUTTON
G RED LIGHT (LOW FLOW)
H RED LIGHT (MACERATOR OVERLOAD)
I AUDIBLE ALARM (ON-OFF)
J EMERGENCY STOP - RESET PUSHBUTTON
K ALARM RESET PUSHBUTTON
L RED LIGHT (OVER PRESSURE)
M RECIRCULATION PUMP (HAND-OFF-AUTO)
N PRESSURE CONTROL PUMP (HAND-OFF-AUTO)
PFX-C-39

Figure 6. Schematic of Superchlorination Process at Rocky Mount and Fayetteville, NC and locations of sampling (Vent No. 1 - Influent, Vent No. 2 - Effluent).



Superchlori-
nation
Process
10
*
9
8
*
7
*6
5
*
4
3
2
1

Figure 7. Sampling locations (asterisks) for settling beds (Nos. 1-10) at the Rocky Mount, NC site.

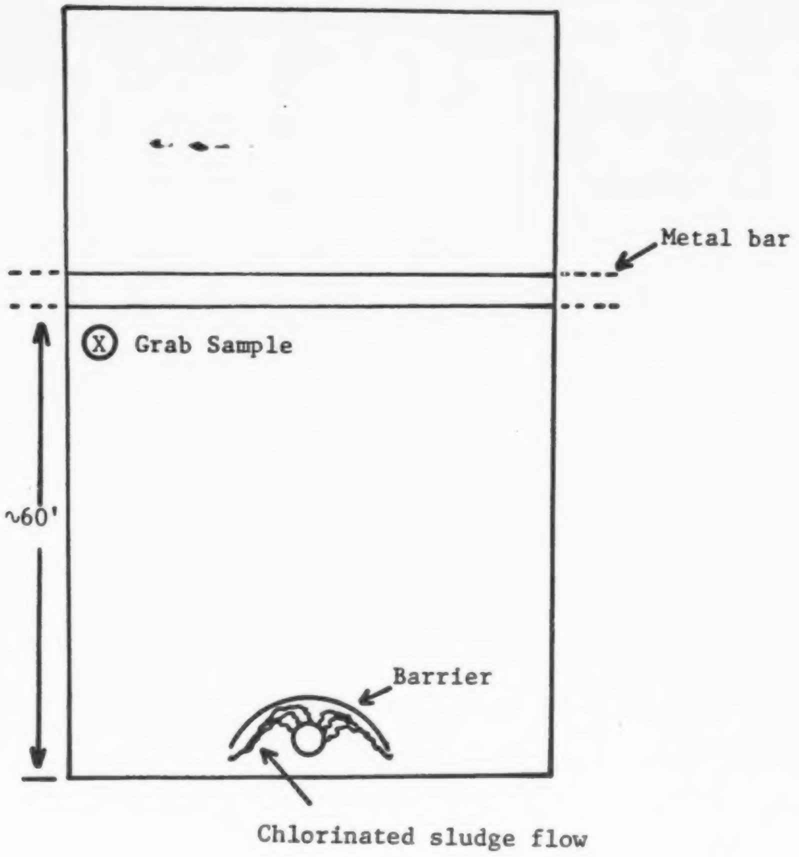

Metal bar
Grab Sample
~60'
Barrier
Chlorinated sludge flow

Figure 8. Chlorinated sludge entering settling bed at Fayetteville Municipal Wastewater Treatment Facility exhibiting where sample was taken.

to wide-mouth quart jars wrapped with an aluminum foil and sealed with Teflon®-lined caps. The sampling protocols for the superchlorination processes at Rocky Mount and Fayetteville, NC are given in Tables 20 and 21.

Chlorine Determination in Samples from Fayetteville Treatment Plant

The total chlorine of each sample was fractionated into the free chloride ion of the supernatant, the organic chlorine content of finely suspended solids and aqueous soluble organics, and the organic chlorine content of insoluble particulates. The latter two fractions necessitate a Schöniger oxidation and collection of water soluble gases prior to analysis (5).

Potentiometric titration of chloride ion with standard silver nitrate using a solid state silver chloride/saturated calomel electrode was the method used. A linear response to chloride ion was established over approximately four orders of magnitude, and a single titration of sodium chloride in deionized water yielded an accuracy of 1.8% relative standard deviation.

The Schöniger method was used for the determination of organic chlorine (5). Seventy-five grams of each sludge was centrifuged (∿2000 rpm) until a tightly packed solid was achieved. Supernatant volumes were determined in a graduated cylinder and then refrigerated in glass amber bottles with Teflon®-lined caps. The solids were resuspended in deionized water, centrifuged and the solids transferred to previously tared crucibles or watch glasses. Residual liquid was allowed to evaporate at ambient temperature for a period of 3 days.

Combustion of 25 to 35 g of each air-dried solid sample was conducted in a 500 mL Schöniger oxidation flask according to the method of Welcher and Ma (5). The flask was allowed to stand a minimum of 1 h after combustion. Samples not immediately analyzed were refrigerated.

The method of standard addition was used with standard sodium chloride to generate regression curves for all supernatant and combusted solids. A minimum of 3 data points was employed for each regression.

Combustion products were acidified with nitric acid and titrated with no dilution. Influent samples also required no dilution. Effluent samples required a 1:100 dilution to achieve an approximately 0.035 g/L concentration to be within the linear response region of the ion specific electrode.

Table 20. SAMPLING PROTOCOL FOR SUPERCHLORINATION PROCESS AT WASTEWATER TREATMENT PLANT IN ROCKY MOUNT, NC[a]

Sample	Code	Sample Type	Sampling Time
RINF	1S1	influent sludge	12:30-12:40
RINF	1S2	influent sludge	12:30-12:40
RINF	2S1	influent sludge	13:25-13:35
RINF	2S2	influent sludge	13:25-13:35
RINF	3S1	influent sludge	14:30-14:40
RINF	3S2	influent sludge	14:30-14:40
REFF	1S1	effluent chlorinated sludge	12:30-12:40
REFF	1S2	effluent chlorinated sludge	12:30-12:40
REFF	2S2	effluent chlorinated sludge	12:30-12:40
REFF	2S1	effluent chlorinated sludge	13:25-13:35
REFF	3S1	effluent chlorinated sludge	14:30-14:40
REFF	3S2	effluent chlorinated sludge	14:30-14:40
RBED	S1	14 day-old chlorinated sludge from settling bed	-
RBED	S2	4 day-old chlorinated sludge from settling bed	-
RBED	S3	1 day-old chlorinated sludge from settling bed	-
RBED	S4	2 hour-old chlorinated sludge from settling bed	13:45

[a] Samples were acquired on June 6, 1979.

Table 21. SAMPLING PROTOCOL FOR SUPERCHLORINATION PROCESS AT WASTEWATER TREATMENT FACILITY IN FAYETTEVILLE, NC[a]

Sample Code	Sample Type	Sampling Time
FINF 1S1	influent sludge	11:10-11:15 AM
FINF 1S2	influent sludge	11:10-11:15 AM
FINF 2S1	influent sludge	12:10-12:12 PM
FINF 2S2	influent sludge	12:10-12:12 PM
FINF 3S1	influent sludge	1:11-1:16 PM
FINF 3S2	influent sludge	1:11-1:16 PM
FEFF 1S1	effluent chlorinated sludge	11:10-11:15 AM
FEFF 1S2	effluent chlorinated sludge	11:10-11:15 AM
FEFF 2P1	effluent chlorinated sludge	12:10-12:12 PM
FEFF 2P2	effluent chlorinated sludge	12:10-12:12 PM
FEFF 3S1	effluent chlorinated sludge	1:11-1:16 PM
FEFF 3S2	effluent chlorinated sludge	1:11-1:16 PM
FBED S1	chlorinated sludge from settling bed	1:00-1:05 PM
FBED S2	chlorinated sludge from settling bed	1:00-1:05 PM

[a] Samples acquired on September 19, 1979.

Twenty to twenty-five mL of influent sludge or chlorinated effluent sludge was titrated.

Standard sodium chloride solution was added to the sample after each endpoint was determined until the change in potential was maximum. Standard sodium chloride solution was initially added to influent samples but not to effluent samples. The liquid sample was vigorously stirred and was shielded from light. Standard silver nitrate solution was added using a buret accurate to ±0.02 mL.

Single endpoint analyses of a standard sodium chloride solution and combusted p-chlorophenoxyacetic acid were conducted. The former yielded a percent relative standard deviation of 1.8%; the latter 5.7%. The increased variability was attributed to the combustion step in this procedure.

Sample Purification

Volatiles--

A modification of the EPA Interim Protocol "V100 - Methods for Purgeable Organics" was utilized (6). A sludge volume equivalent to 50 mg dry solids determined by evaporation and weighing of four 2 mL homogeneous aliquots was added to sufficient deionized water (previously purged with helium at 40 mL/min for 16 min) in a 10 mL Bellar apparatus to give a final volume of 10 mL. The Bellar apparatus was then capped with a 1.5 cm x 6.0 cm Tenax GC® sorbent cartridge and its contents were purged for 12 min with helium at 40 mL/min. The cartridge was then transferred to a foil wrapped Kimax® culture tube containing calcium sulfate previously baked for 4 h at 400°C, sealed with Teflon®-lined caps and then analyzed by GC/MS.

Semivolatiles--

The EPA Interim Protocol"B100 Method for Semivolatile Organic Components" was followed with minor modifications (7).

Extraction--

Solvent and blanks from the extraction procedure for both acid/neutrals and bases were processed according to the protocol.

Acids and Neutrals--Four 25 g aliquots of representative liquid sludge were transferred to 50 mL centrifuge tubes with Teflon®-lined caps and acidified with 1.45 g of hydrated potassium bisulfate. Each tube was extracted three times with 25 mL of distilled methylene chloride for 5 min on a shaker and then centrifuged. The combined methylene chloride extracts were filtered through glass wool into receiving flasks. Extracts were dried over sodium sulfate which had been previously extracted with pentane.

Bases--Five g of thoroughly mixed liquid sludge was buffered with 10 mL of 0.1N H_2PO_4/HPO_4 in a 50 mL centrifuge tube sealed with a Teflon®-lined cap and twice extracted with CH_2Cl_2 followed by centrifugation with 5 mL of redistilled chloroform. The combined solvent extracts were dried over sodium sulfate. Extracts were twice extracted with 2N sulfuric acid solutions for 5 min in culture tubes equipped with Teflon®-lined caps. Aqueous extracts were neutralized by addition of 1.0 mL of 0.4N sodium phosphate and dropwise addition of 20% ammonium hydroxide. The organics were partitioned into two 10 mL chloroform extracts which were then washed with 5 mL of distilled water, dried over sodium sulfate, concentrated in a Kuderna-Danish (K-D) apparatus to 0.4 mL, gently blown down to 0.2 mL under ambient nitrogen, and then analyzed by GC/MS.

Acid and Neutrals--Methylene chloride extracts were concentrated to ~70 mL, partitioned with 200 mL of petroleum ether (Burdick and Jackson) using three successive 400 mL portions of 0.1N sodium hydroxide/10% sodium chloride in a 1 L separatory funnel, then twice with 200 mL 10% sodium chloride. The organic layer was dried over sodium sulfate. The fraction was then concentrated to <200 mg/mL of soluble organics for GPC analysis.

Preparation of Gel Permeation Chromatography--A 1.3 cm x 110 cm Chromatronix column was packed with biobeads SX-8 previously swelled in methylene chloride such that the required operating flow did not exceed 15 psi. An FMI pulseless pump was adapted for upward flow and detection was achieved by a UV photometer [(254 nm) mercury ultraviolet lamp].

Standard solutions were used which established the GPC windows for fractionation of the acid and neutral extracts previously prepared.

Calibration Solution--A methylene chloride solution containing approximately 45 μg/mL of corn oil and ~2 μg/mL of di-n-octyl phthalate, dimethyl phthalate, p-chlorophenyl phenyl ether, pyrene, and sulfur was employed to establish windows for the neutral fractions from the GPC column. The components eluted in the order described. Fraction 1 (NF1) of each extract was collected as the minima between the corn oil/octyl phthalate and dimethyl phthalate/p-chlorophenyl phenyl ether sets. Fraction 2 (NF2) was collected as the remaining elements up to the pyrene/sulfur minimum.

A methylene chloride solution containing approximately 2 μg/mL each of n-octanoic acid, 2,4-dimethylphenol, 2,4-dinitrophenol, and sulfur was employed to establish windows for the acid fraction. The elution order was as described. The acid fraction (AF1) was taken as the minima of the n-octanoic acid/dimethylphenol and the dinitrophenol/sulfur sets.

Operating Conditions--Two mL injections of both standards and samples were made via a three way valve connecting a 10 mL glass jacket-Teflon® barrel syringe to the system pump and GPC column. Repeated calibrations with continual monitoring and maintenance of degassed methylene chloride flow at 1 mL/min indicated the existence of moderately reproducible windows (1-2 min). Column efficiency was a function of a given calibration run and varied from 850-1950 theoretical plates from one GPC column to another.

The previously extracted acids/neutral effluent and bed samples were concentrated to ~2 mL in a micro K-D apparatus containing uncoated glass capillary fragments to minimize bumping. Following calibration of the system, a 2 mL aliquot of extract was directly injected onto the column. Liquid fractions were collected in 250 mL centrifuge tubes previously washed and oven dried.

Dry sample remaining in the syringe or transfer line to the three way valve was diluted with methylene chloride to 2 mL and injected as a record run. Sample remaining in the transfer line after this dilution was then removed and disposed.

Workup of Extracts and GPC Fractions--

Neutrals in GPC Fraction--Fraction 1 (NF1) was concentrated to 2 mL, diluted to 4 mL with petroleum ether and transferred to an 8 x 900 mm chromatography column (with Teflon® stopcock) packed with 20 g activated Grade 923 silica previously washed with 50 mL of 25% acetone/methylene chloride and 50 mL of petroleum ether. The fraction was eluted with 50 mL of 50% pet ether/methylene chloride and 50 mL of 25% acetone/methylene chloride. The latter fraction was combined with fraction 2 (NF2) from the GPC run and concentrated to ~6 mL. The extract was then transferred to a micro K-D with ~1 mL of ethylene dichloride. The fractions were then concentrated to ~500 μL and 10 μg of d_{10}-anthracene was added. Solvent exchange with tetrahydrofuran was then necessary for GC/MS analysis.

Pre- and post-GPC column fractions and their corresponding blanks were concentrated to approximately 500 μL and then subjected to GC/MS analysis. Preparation of the neutral window fraction for analysis requires fractionation of the first of two collected fractions onto silica gel. An eluant of an intermediate polarity (25% acetone in methylene chloride) was collected with the disposal of a non-polar (50% pet. ether in methylene chloride) fraction. The first window fraction of Effluent No. 1 was regenerated with the retention of this non-polar eluant for analysis. The column was then flushed with acetone to collect a polar fraction for GC/MS analysis. The final solvents for the fractions were, respectively, THF and acetone.

Acids in GPC Fractions--The GPC fractions were concentrated to approximately 3 mL and partitioned between 20 mL of hexane and 20 mL of 0.1N NaOH/10% in a 50 mL culture tube equipped with a Teflon®-lined cap. The partitioned extracts were then oscillated on a floor shaker for 20 min, after which time the basic fraction was isolated and the extraction repeated. The combined basic fractions were acidified with 6N HCl and twice partitioned into methylene chloride. The organic extracts were dried over extracted sodium sulfate, filtered into a K-D apparatus, concentrated to ~5 mL, and transferred to a micro K-D with approximately 1 mL of ethylene dichloride. Concentration was continued to approximately 500 μL and 10 μg of d_{10}-anthracene was added. Solvent exchange with tetrahydrofuran was then performed.

In addition to the collection of acid and neutral fractions that eluted from the gel permeation column within the previously established window, fractions prior to and following these windows were also collected for GC/MS analysis. All seven acid window fractions and one blank were prepared according to the protocol.

One fraction of a neutral extraction was subjected to removal of polar and non-polar interferences via silica gel chromatography. In the conventional Priority Pollutant protocol, these fractions are normally discarded; however, these fractions were kept for GC/MS analysis. Since the solvents methylene chloride or ethylene dichloride are incompatible with analysis by negative ion chemical ionization, a solvent exchange was conducted of all the extracts with the final solvent of choice being tetrahydrofuran.

The pre- and post-column fractions of influent and effluent numbers 2 and 3 and the corresponding blanks were concentrated to ~2 mL and subjected to basic extraction and acidification per the protocol established for the window acid fraction. The organic extracts were concentrated to approximately 300 to 400 mL and 100 μL of N-methyl-N-trimethylsilyl trifluoroacetamide (MSTFA) were added. The extracts were allowed to stand overnight at ambient temperature to allow derivatization to occur. The window fraction of sample effluent No. 1 was regenerated and silanized to observe any disparity between silanized and unsilanized detection limits.

Analysis of the supernatant of Effluent No. 1 via the method of standard addition yielded an excellent fit for a least squares analysis and an extrapolated concentration of 0.143$\underline{N}$ in chloride ion. A repeat analysis yielded 0.141$\underline{N}$; thus, an average of 0.142$\underline{N}$ in Cl was observed.

Instrumental Analysis

The samples were analyzed on an LKB 2091 (PDP 11/04 Data System) gas chromatograph/mass spectrometer/computer system utilizing both electron impact and negative ion chemical ionization. The use of negative chemical ionization was especially useful since it is highly selective and sensitive to electron capturing compounds. Because many chlorinated compounds possess a high electron capture coefficient, they would be particularly amenable to negative ion chemical ionization. Tables 22 and 23 present the GC/MS conditions for acid and other fractions, respectively. The neutral fractions were chromatographed on a 25 m wall coated open tubular column (fused silica) coated with SP-2100 phase. These fractions were also chromatographed on a conventional 6 ft 1% SP-2250 coated packed column. The acid fractions were analyzed on a 6 ft packed column containing 1% SP-1240 DA.

RESULTS AND DISCUSSION

Organic Chlorine Concentration

A study of the linearity of detection indicated that a wide scattering for influent sludge titrations may result from interferences not encountered in the highly diluted chlorinated effluent sludge samples. Negative and positive intercepts of the abscissa were obtained with the application

Table 22. GC/MS CONDITIONS FOR FAYETTEVILLE ACID FRACTIONS

Parameter	Positive ion	Negative ion
Ion source temperature	210°C	210°C
Electron energy	70 eV	50 eV
Trap/box current	50 µA	250 µA
Reagent gas	-	Methane
Reagent gas pressure	-	4×10^{-5} T
Accelerating voltage	3500 V	3500 V
Scan interval	2.0 sec	2.5 sec
Column	1.82 m 1% SP1240 DA	1.82 m 1% SP1240 DA
Temperature program	85°C/1 min then 10°C/min to 200°C	85°C/min then 10°C/min to 200°C
Helium flow	14.0 mL/min	14.0 mL/min
Injector temperature	220°C	220°C
Separator temperature	210°C	210°C

Table 23. GC/MS CONDITIONS FOR OTHER FAYETTEVILLE FRACTIONS

Parameter	Positive ion		Negative ion	
Ion source temperature	250°C		250°C	
Electron energy	70 eV		50 eV	
Trap/box current	50 μA		250 μA	
Reagent gas	-		Methane	
Reagent gas pressure	-		4×10^{-5} T	
Accelerating voltage	3500 V		3500 T	
Scan interval	2.0 sec		2.0 sec	
Column	25 M SP2100 WCOT (Hewlett-Packard) and	1.85 m 1% SP2250	25 M SP2100 WCOT and	1.85 m 1% SP2250
Temperature program	50°C for 4 min then 8°/min to 260°C for 20 min	50°C/4 min then 8°/min to 260°C/ 20 min	50°C/4 min, 8°/min to 20 min	50°C/4 min 8°/min to 260°C/20 min
Helium flow	.73 mL/min	14.0 mL/min	.73 mL/min	14.0 mL/min
Injector temperature	220°C	250°C	220°C	250°C
Separator temperature	250°C	275°C	250°C	275°C

of linear regression to the influent data. Thus, an ultimate detection limit was estimated.

The linear regressions for the influent sludge combustion products all yielded positive abscissa intercepts and supported the proposition of interferences. The mean of these positive intercepts was taken as a chloride ion equivalent detection limit. The value based upon these three samples was $6 \pm 3 \times 10^{-6}$ equivalents of chloride ion. The percentage of chloride ion detection limit for the combusted solids based on these values was 0.6 ± 3% (% standard deviation).

The 20 mL of Schöniger adsorption solution after combustion approached the 25 mL volume of supernatant titration. Thus, it was not unreasonable to employ the solid limit of detection to establish the supernatant limit of detection. For a 25 mL sample, the numerical value was $8.3 \pm 1.2 \times 10^{-3}$ g/L of chloride ion.

Two of the three influent supernatants approached the abscissa asymptotically and indicated a greater chloride content than a linear regression. However, the greater of the two values, 2.45×10^{-2} g/L, is less than an order of magnitude and may be taken as the upper limit of influent chloride ion content.

The values presented in Table 24 may be the upper chloride ion concentrations limits since interfering species may also precipitate silver ion.

The results for the organic chlorine content for superchlorinated sludges and supernatants obtained from the Fayetteville, NC plant are given in Table 24.

Identification Measurement of Chlorinated Compounds

Rocky Mount (Pilot Study)--

Extracts of samples from the superchlorination process were analyzed by GC/MS/COMP using electron impact and negative ion chemical ionization modes. Table 25 presents the results for the purgeable chlorinated compounds identified in an influent sludge and chlorinated effluent sludge from the process.

Tables 26 through 29 lists the chlorinated substances which were identified in the extract fractions of the immediate effluent and sludge (from the settling pond). Several chlorinated hydroxybenzene analogs were detected

Table 24. ORGANIC CHLORINE CONTENT FOR FAYETTEVILLE, NC SUPERCHLORINATED SLUDGES

Sample Code	Supernatant	Solid
FINF 1S1	$\leq 7 \times 10^{-4}$ $\underline{N}$[a]	<0.6 ± 0.3%
FINF 2S2	$\leq 7 \times 10^{-4}$ $\underline{N}$	<0.6 ± 0.3%
FINF 3S2	$\leq 7 \times 10^{-4}$ $\underline{N}$	<0.6 ± 0.3%
FEFF 1S1	0.138N, 0.143N	5.28%
FEFF 2S2	0.132N	2.15%, 2.28%
FEFF 3S2	0.086N	2.99%
FBED S1	0.107N	4.50%

[a] Expressed as equivalents of chloride ion.

Table 25. "PURGEABLE" CHLORINATED COMPOUNDS IDENTIFIED IN EFFLUENT FROM A SUPERCHLORINATION AT ROCKY MOUNT, NC FACILITY[a]

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1	44	CO_2
2	49	chloroethane
3	54	methylene chloride
4	63	hexafluorobenzene (eS)
5	64	chloroform
6	67	perfluorotoluene (eS)
7	72	carbon tetrachloride
8	78	trichloroethylene
9	101	tetrachloroethylene
10	107	chlorobenzene
11	138	dichlorobenzene isomer (trace)
12	168	trichlorobenzene isomer (traces)

[a] Sample taken at the immediate outlet from superchlorination process (1230-1240 h, 6/6/79).

Table 26. CHLORINATED COMPOUMDS IDENTIFIED IN THE NEUTRAL FRACTION OF EFFLUENT FROM THE SUPERCHLORINATION AT ROCKY MOUNT, NC FACILITY[a]

Peak No.	Elution Temperature	Compound
1	65	solvent
2	109	trichlorobenzene isomer
3	162	dichlorobenzoic acid isomer (tent.)
4	171	chlorinated compound (unknown)

[a] Sample taken at immediate outlet from the superchlorination process (1325-1335 h, 6/6/79).

Table 27. CHLORINATED COMPOUNDS IDENTIFIED IN THE ACID FRACTION OF EFFLUENT FROM THE SUPERCHLORINATION AT ROCKY MOUNT FACILITY[a]

Peak No.	Elution Temperature	Compound
1	161	dichlorocresol isomer
2	162	chloroamylphenol isomer (tent.)
3	178	alkyl chlorophenol isomer
4	199	chlorinated compound (unknown)
5	200	methylchlorohydroxybiphenyl isomer (tent.)

[a] Sample taken at immediate outlet from the superchlorination process (1325-1335 h, 6/6/79).

Table 28. CHLORINATED COMPOUNDS IDENTIFIED IN THE NEUTRAL FRACTION OF SLUDGE FROM SETTLING BED OF THE SUPERCHLORINATION AT ROCKY MOUNT, NC FACILITY[a]

Peak No.	Elution Temperature (°C)	Compound
1	60	1,2-dichloroethane
2	60	dichloromethane
3	122	chlorinated compound (unknown, trace)
4	160	dichlorobenzoic acid isomer
5	177	chlorinated compound (unknown)
6	177	chlorinated compound (unknown)
7	185	chlorinated compound (unknown)

[a] Sample was taken from a 2 h old settling bed (1345 h, 6/6/79).

Table 29. CHLORINATED COMPOUNDS IDENTIFIED IN THE ACID FRACTION OF SLUDGE FROM SETTLING BED OF THE SUPERCHLORINATION PROCESS AT ROCKY MOUNT, NC FACILITY[a]

Peak No.	Elution Temperature (°C)	Compound
1	121	2,3-Dichloropropanol-1 (tent.)
2	134	6-Chloro-*o*-cresol or Methylchlorophenol isomer
3	160	4,6-Dichloro-*o*-cresol or Dichlorocresol isomer
4	161	C_5-Alkyl chlorophenol isomer (tent.)
5	169	Trichlorophenol isomer
6	178	Alkyl chlorophenol isomer
7	184	Alkyl chlorophenol isomer
8	197	Chloro compound (unknown)
9	200	Methylchlorohydroxybiphenyl isomer (tent.)

[a] Sample was taken from a 2 h old settling bed (1345 h, 6/6/79).

and further confirmed by negative ion chemical ionization GC/MS. However the levels of these compounds were very low. Sample extracts which were derivatized did not reveal new components.

Table 30 gives the measured levels of "purgeable" organics in the sludge samples. Comparison of the levels of the selected purgeable organics between the influent and chlorinated effluent sludges indicates that several compounds increased appreciably. These compounds were chloroform, carbon tetrachloride, and p-chlorotoluene (Table 24). The concentrations of the remaining organics which were measured in these samples did not appear to increase in concentration after the superchlorination process.

Fayetteville, NC--

Table 31 lists the extracts and fractions generated during processing of samples from the Fayetteville, NC site.

GC/MS/COMP utilizing both electron impact and negative chemical ionization modes were employed for the analysis of fractions derived from the samples taken at the Fayetteville, NC site. Figures A1 through A106 (Appendix A) present the profiles which were obtained for the various influent and effluent samples that were fractionated into "acids"/"neutrals" and bases. Figures A1 through A3 present the results for a solvent blank chromatographed, on a fused silica capillary. The total ion profiles and single ion profiles are also presented in these figures.

Figures A4 through A6 present the results for the neutral fractions for Influent No. 2 to the superchlorination process. Virtually no components were detected in the electron impact mode; however, a small number of components were detected in the negative ion chemical ionization mode (Fig. A5 and A6). In Figure A6 the single ion profiles represent the isotopic forms 35 and 37 for chlorine and 79 and 81 for bromine. From the single ion profiles of Figure A6, it is readily evident that a few peaks were detected which were chlorinated compounds. Figures A7 through A9 present the results of the neutral fraction for Influent No. 3. Again very few chlorinated compounds were detected.

In contrast, the analysis of a neutral fraction for Effluent No. 1 from the superchlorination process indicated the presence of many chlorinated compounds as depicted in Figures A10 through A12. Similarly, the

Table 30. LEVELS OF SELECTED "PURGEABLE" ORGANICS IN LIQUID SLUDGE BEFORE AND AFTER SUPERCHLORINATION AT THE ROCKY MOUNT, NC FACILITY[a]

Compound	ppb[b]						
	RINF/1S	REFF/1S	RINF/2S	REFF/2S	RINF/3S	REFF/3S	Bed Samples
Chloromethane	20 ± 15	32 ± 9	54 ± 32	15 ± 1	18 ± 8	11 ± 5	27 ± 5
Dichlorodifluoromethane	8 ± 8	27 ± 8	4 ± 4	20 ± 4	12 ± 4	17 ± 7	14 ± 1
Bromoethane	3 ± 2	T	T	T	ND	T	T
Methylene chloride	260 ± 110	376 ± 12	203 ± 40	264 ± 27	301 ± 24	267 ± 67	338 ± 28
Trichlorofluoromethane	390 ± 229	118 ± 26	74 ± 26	276 ± 86	223 ± 154	212 ± 78	135 ± 50
1,1-Dichloroethylene	10 ± 3	16 ± 2	9 ± 1	15 ± 3	30 ± 1	12 ± 3	15 ± 5
1,1-Dichloroethane	24 ± 22	39 ± 10	41 ± 41	32 ± 6	17 ± 14	18 ± 7	15 ± 4
Freon 113	15 ± 2	14 ± 1	11 ± 0	15 ± 5	13 ± 2	19 ± 8	12 ± 1
Chloroform	9 ± 7	1,037 ± 140	6 ± 5	1,104 ± 125	6 ± 1	912 ± 312	490 ± 110
1,1,1-Trichloroethane	175 ± 51	211 ± 23	69 ± 34	179 ± 17	2 ± 1	130 ± 55	86 ± 28
Carbon tetrachloride	ND	847 ± 47	ND	989 ± 135	2 ± 2	792 ± 317	395 ± 140
Bromodichloromethane	ND	ND	ND	6 ± 4	ND	T	ND
trans-1,3-Dichloropropene	ND	9 ± 7	ND	10 ± 8	T	22 ± 20	T
Trichloroethylene	86 ± 5	81 ± 1	66 ± 1	85 ± 10	69 ± 13	79 ± 14	73 ± 18
Benzene	50 ± 23	48 ± 20	354 ± 279	39 ± 11	61 ± 24	38 ± 15	45 ± 12
1,1,2,2-Tetrachloroethene	139 ± 32	182 ± 18	102 ± 24	149 ± 10	36 ± 1	92 ± 27	106 ± 34
1,1,2,2-Tetrachloroethane	ND	ND	ND	T	ND	ND	ND
Toluene	778 ± 64	1,213 ± 66	1,432 ± 127	739 ± 14	6,710 ± 154	1,187 ± 357	2,165 ± 644
Chlorobenzene	ND	15 ± 1	11 ± 11	16 ± 1	T	8 ± 7	12 ± 2

(continued)

Table 30 (cont'd.)

Compound	ppb[b]						
	RINF/1S	REFF/1S	RINF/2S	REFF/2S	RINF/3S	REFF/3S	Bed Samples
Ethylbenzene	9 ± 8	13 ± 1	6 ± 6	12 ± 0	19 ± 0	12 ± 1	14 ± 0
p-Chlorotoluene	ND	951 ± 90	T	1,586 ± 269	7 ± 4	1,620 ± 533	762 ± 273
Dichlorobenzene isomer	11 ± 10	25 ± 1	9 ± 9	32 ± 1	33 ± 2	26 ± 8	23 ± 8

[a] See Table 20 for sampling protocol, INF = influent liquid sludge, EFF = effluent liquid sludge.

[b] Based upon total sample.

Table 31. EXTRACTS AND FRACTIONS PRODUCED DURING SAMPLE PROCESSING FOR EXTRACTABLES (FAYETTEVILLE, NC)

Sample Code	Acids			Neutrals					Bases
	Pre-window (GPC)	Window (GPC)	Post-window (GPC)	Pre-window (GPC)	Window (GPC)	Post-window (GPC)	Nonpolar (Silica)	Polar (Silica)	
INF1	GPA-1	"Acids"	GPA-3	GP1	"Neutrals"	GP4	S1	S3	Bases
INF2	GPA-2	"	GPA-3	"	"	"	"	"	"
INF3	GPA-1	"	GPA-3	"	"	"	"	"	"
EFF1	GPA-1	"	"	"	"	"	"	"	"
EFF2	GPA-1	"	"	"	"	"	"	"	"
EFF3	GPA-1	"	"	"	"	"	"	"	"
BED	GPA-1	"	"	"	"	"	"	"	"

chromatograms of neutral fraction for Effluent No. 2 are given in Figures A13 through A15 and again many chlorinated hydrocarbons were detected, particularly when the negative ion chemical ionization mode was employed. For Effluent No. 3 only a few compounds could be detected in the electron impact mode; however, using negative ion chemical ionization MS many chlorinated organics were uncovered (Fig. 16-18).

A sample from the settling bed for the superchlorination process was analyzed and the results for the neutral fraction are given in Figures A19 through A21. Again chlorinated organics were detected as clearly shown in Figures A20 and A21; however, their concentrations appeared considerably lower than those in the immediate effluent from the process.

The acid fraction was also analyzed in the electron impact and negative ion chemical ionization modes for each of the influent and effluent samples. The results for the acid fraction for the Influent Nos. 1-3 are given in Figures A22 through A30. Several chlorinated organics were detected. These compounds appeared at different retention times than those which were detected in the electron impact mode and thus it was concluded that the early eluting chromatographic peaks in Figure A22 were predominately non-chlorinated compounds. These observations were verified when the electron impact/positive ion mass spectra of these chromatographic peaks were examined. Influent Nos. 1-3 are contrasted by Effluent No. 1, i.e., the acid fraction results are given in Figures A31 through A33. Again, many chlorinated organics were detected in this sample. The early eluting peaks in Figure A31 were predominantly non-chlorinated organics; however, minor chlorinated components did appear at those chromatographic retention times. Similar results were obtained for the acid fractions obtained from Effluent Nos. 2 and 3 (Fig. A34-A39). The chromatographic profiles for the acid fraction obtained from the settling bed sample from the superchlorination process were very similar to those obtained for the effluents (Fig. A40-A42). The chromatograms for the acid solvent blank contained trace chlorinated impurities (Fig. A43-A45).

In addition to the fractions which are routinely generated for the analysis of sludge samples by the standard currently available Priority Pollutant protocol, the fractions which are normally excluded by the protocol were analyzed. The results for the GP1 neutral fraction for Influent No. 2 are given in Figures A46-A48. Several chlorinated organics were detected in this fraction prior to the superchlorination process. The GP4 neutral fraction for the sample Influent No. 2 sample was also analyzed by chromatographing the sample on an SP-2100 coated fused silica capillary (A49-A51). The results for the GP4 neutral fraction for Influent No. 3 sample are given in Figures A52-A54. Few chlorinated organics were detected. In contrast, the GP1 neutral fraction for Effluent No. 2 and the GP4 neutral fraction for the same effluent indicated the presence of many chlorinated organics (see Figures A55-A60). Similar results were obtained for the GP1 and GP4 neutral fraction for Effluent No. 3 (see Figures A61-A66). Chromatograms for the GP1 and GP4 neutral fractions are depicted in Figures A67-A72.

Finally, the profiles depicted in Figures A73-A100 present the results for the acid fraction for Influent Nos. 1-3 Effluent Nos. 1-3 and Blanks (GP1 and GP4) chromatographed on the SP-1240 DA packed column. Again many chlorinated organics were detected.

Additional fractions which are not included as part of the analysis when using the Priority Pollutant protocol were examined for the presence of chlorinated organics in the influent and effluent from the superchlorination process. The S1 neutral THF fraction for Effluent No. 1 and the S3 neutral/acetone fraction of effluent No. 1 from the superchlorination process were analyzed and the results are given in Figures A101-A106. As indicated in the chromatographic profile for these samples analyzed by negative ion chemical ionization, many chlorinated organics were detected.

Because chlorinated cyclohexene derivatives could be formed as artifacts of the work-up of the samples and since the extraction solvent, methylene chloride, contains ∿1% cyclohexene as a preservative, the residual chlorine in the samples was quenched. Figures A107-A110 present the negative ion chemical ionization profiles for the neutral fraction of Effluent No. 2 from the superchlorination process which was divided into two aliquots. One had been quenched with sodium thiosulfate (0.026 moles) in excess of the amount of chlorinated material determined in these samples while the other aliquot was not quenched. These two aliquots of Effluent No. 2 were then processed according to the current Priority Pollutant protocol to generate the neutral fraction. These results indicate slight differences between two aliquots and examination of the mass spectra (negative ion chemical ionization) indicates that a number of the chlorinated cyclohexanes and cyclohexanols are absent in the chlorine-quenched sample. This is consistent with the previous studies which have indicated that methylene chloride when used in the Priority Pollutant protocol in the extraction of neutral compounds can have an appreciable quantity of cyclohexene which may become readily chlorinated in the presence of molecular chlorine in a water sample. The aliquot which had been treated with sodium thiosulfate after organic extraction and centrifugation had a yellow color and a characteristic sulfur odor. Attempts to concentrate the organic extract of the thiosulfate-treated sample to two milliliters for injection onto the gel fractionation column were complicated by copious precipitation of low solubility sulfur. A majority of the solid was removed by cooling the extract in a dry ice/acetone bath and filtering it through a glass pipet containing glass wool. Nevertheless, the number of peaks attributable to this artifact are few and the overwhelming majority are apparently chlorinated materials which are appearing in the effluent from the superchlorination process and not as an artifact of the storage and workup of the sample.

Table 32 presents the differences between the unquenched and quenched sample with regard to chlorinated cyclohexane derivatives.

An attempt was made to identify the chlorinated compounds present in the neutral and acid fractions for the influent, effluent and settling bed samples. These results are given in Tables 33 and 34. Considerable difficulty was experienced in the identification of these compounds since their concentrations were seemingly below the detection limit for electron impact positive ion mass spectrometry and the fragmentation pattern for these compounds in the negative ion chemical ionization mode was extremely simple which precluded the identification of many constituents. Nevertheless, some of the chlorinated materials have been identified.

Table 32. COMPARISON OF CHLORINATED CYCLOHEXANES IN CHLORINE QUENCHED AND UNQUENCHED SUPERCHLORINATION PROCESS SAMPLES

Compound	Quenched	Unquenched
Chlorocyclohexane	-	-
Chlorocyclohexanol	-	+
Dichlorocyclohexane(s)	-	+

Table 33. CHLORINATED COMPOUNDS IDENTIFIED IN FAYETTEVILLE, NC - NEUTRAL FRACTIONS

Fraction	Spectrum Number	Compounds	Negative[a] Ion		Positive[b] Ion	
			A	B	C	B
INF 2	606	pentachlorotoluene	X			
	700	$C_7H_3Cl_5O$	X			
INF 3	610	pentachlorotoluene	X			
	788	tetrachlorobiphenyl	X			
	702	$C_7H_3Cl_5O$	X			
Bed	607	pentachlorotoluene	X			
	700	$C_7H_3Cl_5O$	X			
EFF 1	808	$C_7H_3Cl_5O$		X		
	843	*p*,*p*'-DDE	X			
	610	pentachlorotoluene	X			
	448	trichloropyridine (tent.)	X			
	426	dichloropyridine (tent.)	X			
EFF 2	203	chlorotoluene			X	
	342	trichloroaniline				X
	267	dichloroaniline				X
	447	trichloropyridine	X			
	701	$C_7H_3Cl_5O$	X			
EFF 3	-	-ND-				
GP1 NEUT EFF 2	372	trichlorotoluene		X		
	426	$C_7H_4Cl_4$		X		
GP1 NEUT EFF 3	372	trichlorotoluene		X		
	424	$C_7H_4Cl_4$		X		
EFF 1-S1 cut/THF	409	pentachlorotoluene		X		
	307	trichlorotoluene		X		

[a] A refers to SP2100 capillary column, B to SP2250 packed column.

[b] C refers to SP2100 capillary column, B to SP2250 packed column.

Table 34. CHLORINATED COMPOUNDS IDENTIFIED IN FAYETTEVILLE, NC ACID FRACTIONS

Fraction	Spectrum number	Compound	Negative ion	Positive ion
EFF 2 acid	279	chlorophenol	X	
	348	chlorophenylacetic acid	X	
	420	trichlorophenol (tent.)	X	

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6. EPA Interim Protocol. "V100-Methods for Purgeable Organics in Sludge". EPA/EMSL/CI, December, 1979.
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APPENDIX A

GC/MS/COMP PROFILES OF FRACTIONS OBTAINED FOR SAMPLES FROM FAYETTEVILLE, NC SUPERCHLORINATION PROCESS

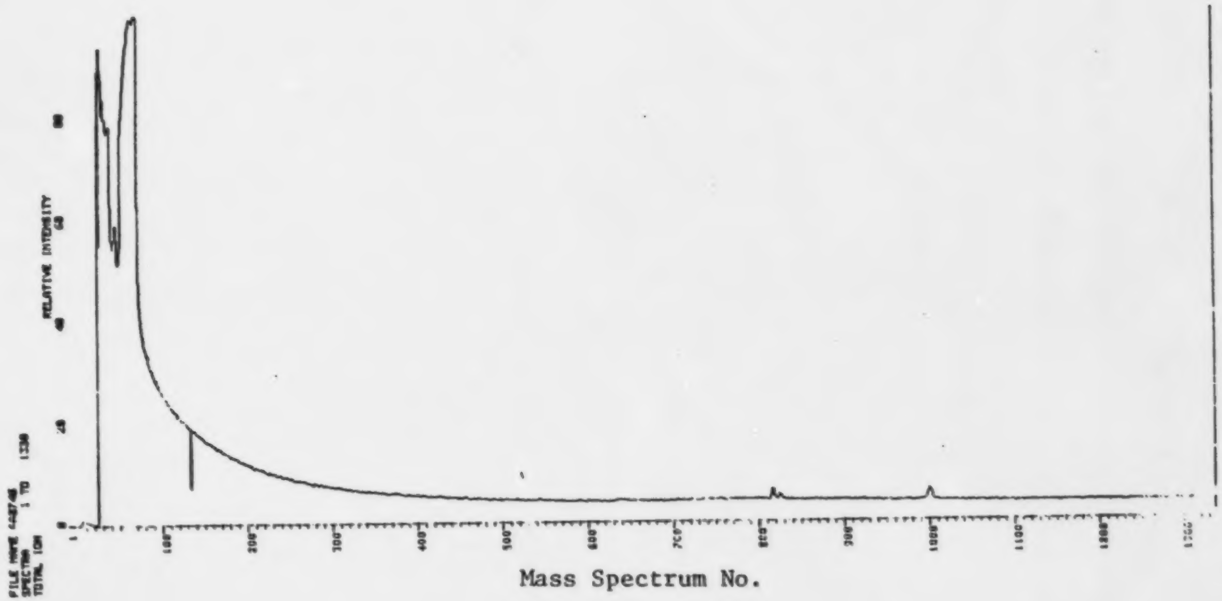


Figure A1. Electron impact GC/MS/COMP profile of solvent blank (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

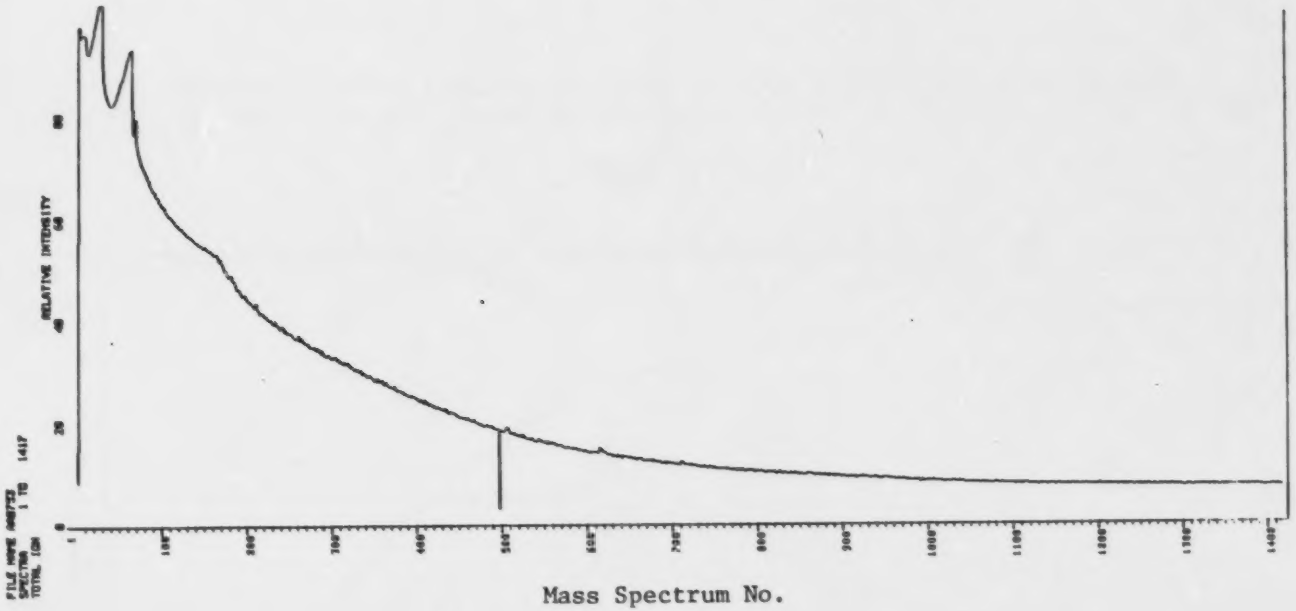
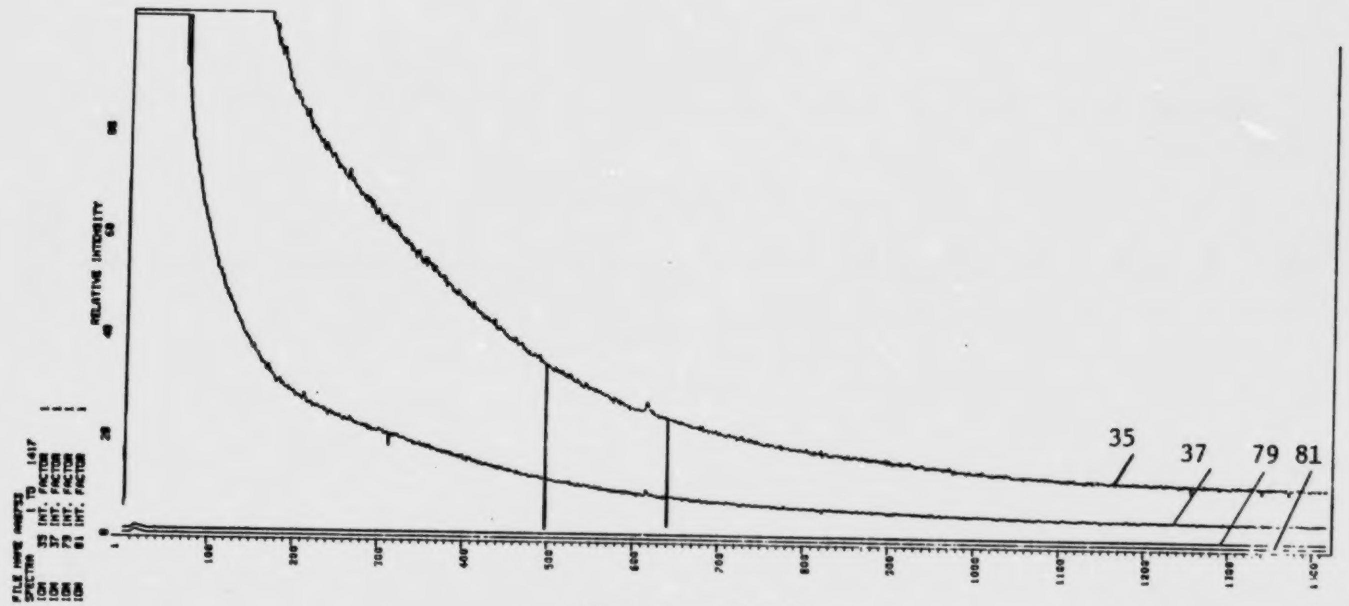


Figure A2. Negative chemical ionization GC/MS/COMP profile of solvent blank (SP2100, 0.23 mm i.d. x 25 m fused silica blank).



Mass Spectrum No.

Figure A3. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of solvent blank (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

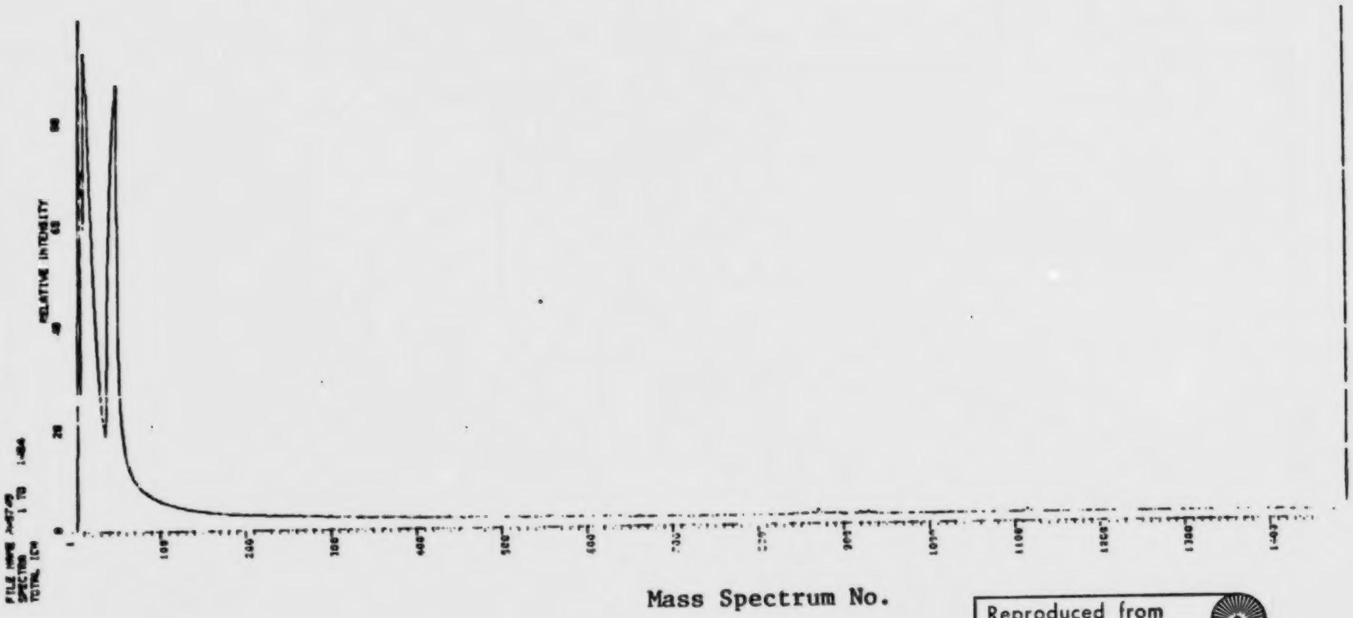


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Figure A4. Electron impact GC/MS/COMP profile of "Neutral" fraction for Influent No. 2 to superchlorination process (SP2100 Hewlett-Packard fused silica capillary - 0.23 mm i.d. x 25 m).

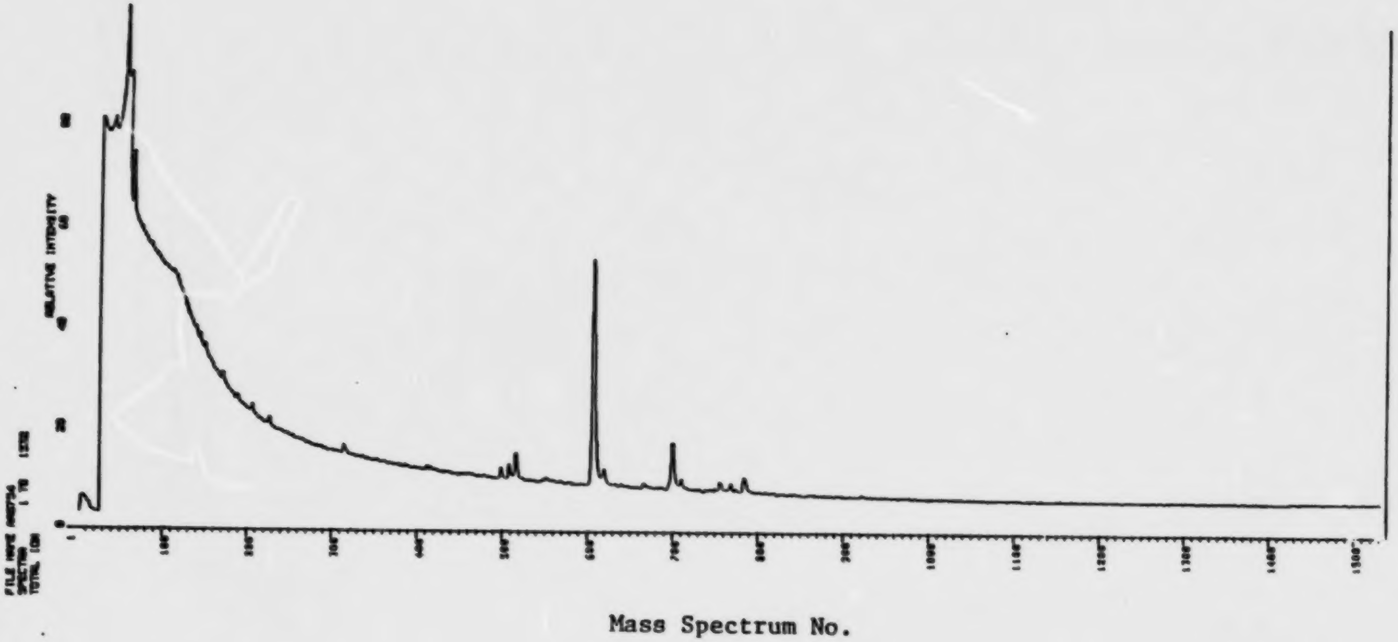

Figure A5. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction of Influent No. 2 to superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

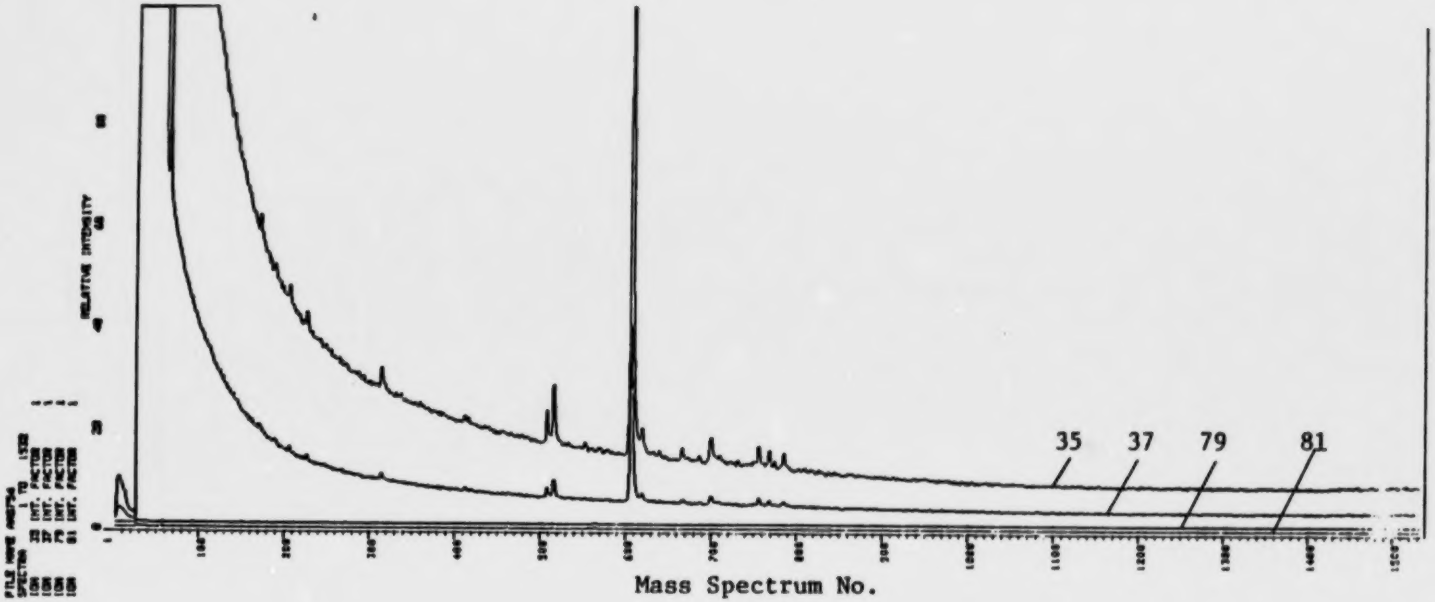

Figure A6. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "neutral" fraction of Influent No. 2 to superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

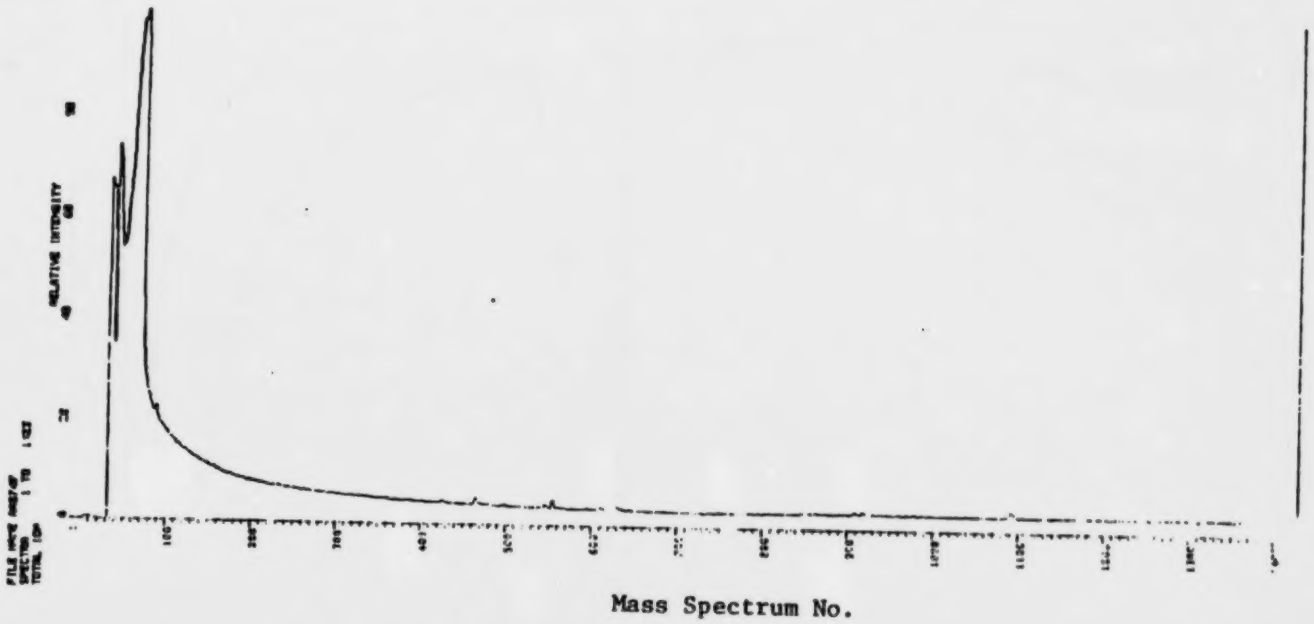

Figure A7. Electron impact GC/MS/COMP profile for "neutral" fraction for Influent No. 3 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

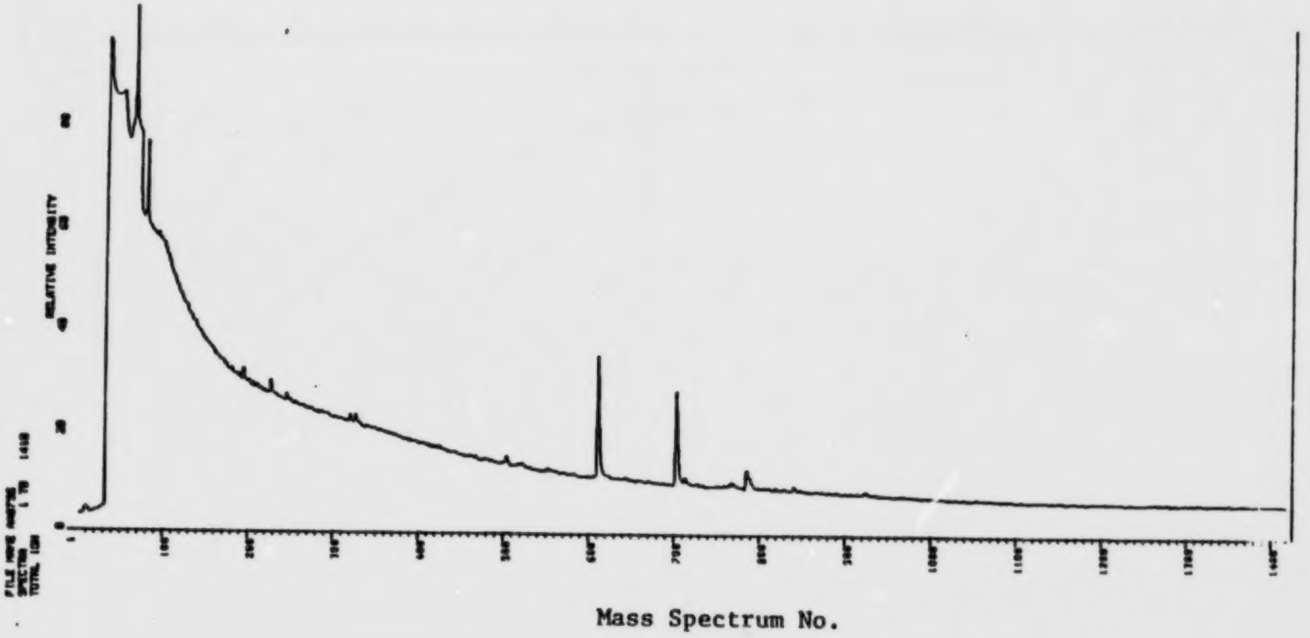

Figure A8. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction for Influent No. 3 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

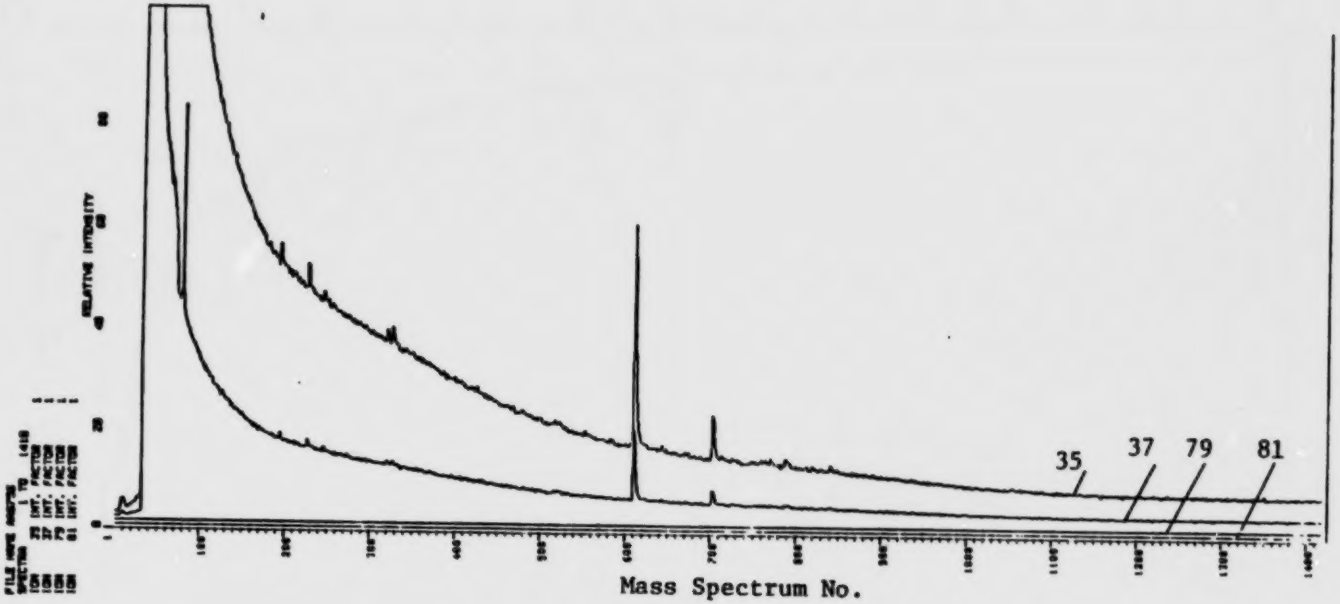

Figure A9. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "neutral" fraction for Influent No. 3 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

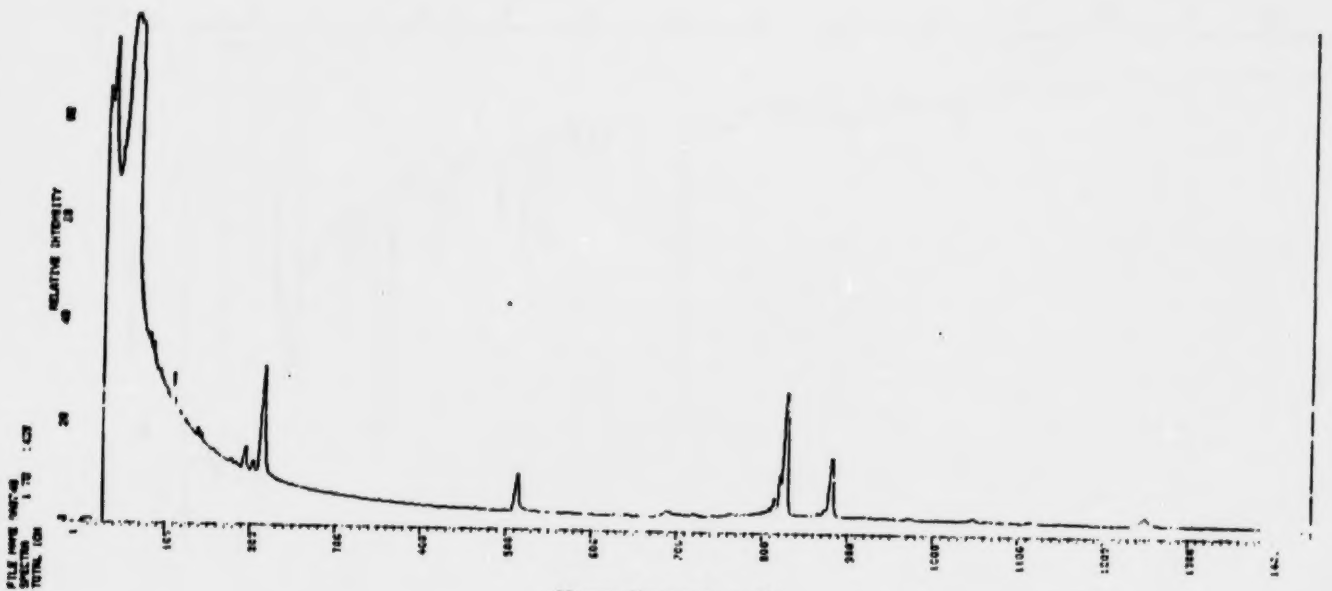

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Figure A10. Electron impact GC/MS/COMP profile of "neutral" fraction for Effluent No. 1 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

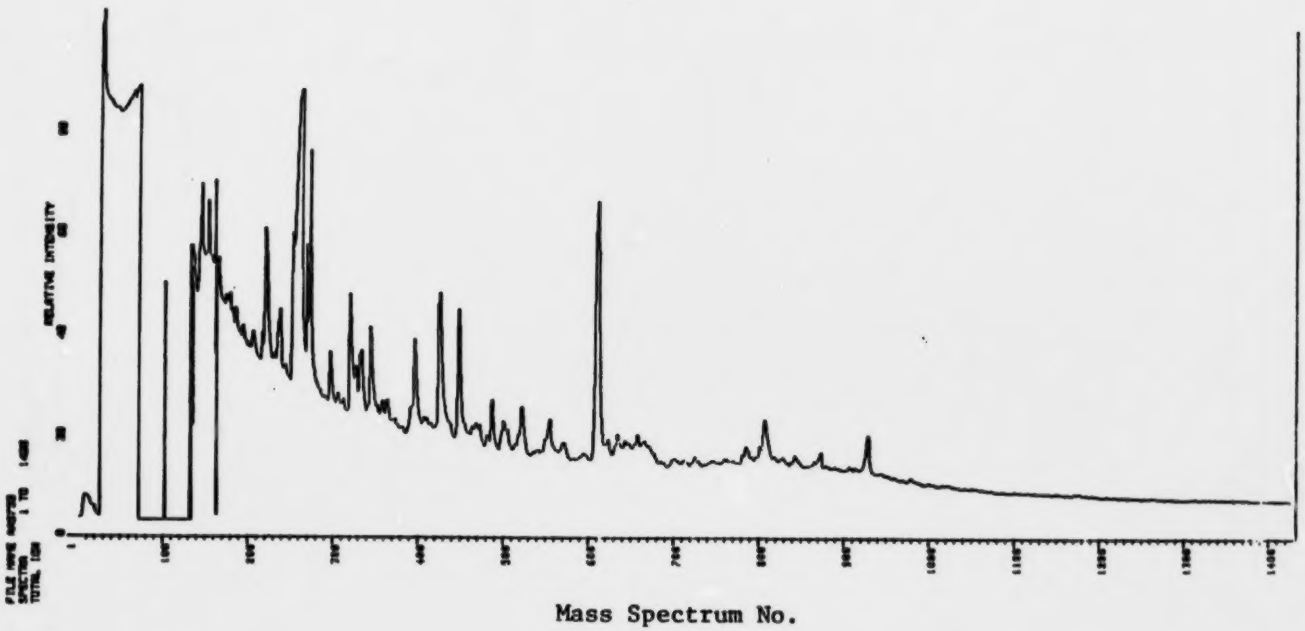

Figure A11. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction for Effluent No. 1 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

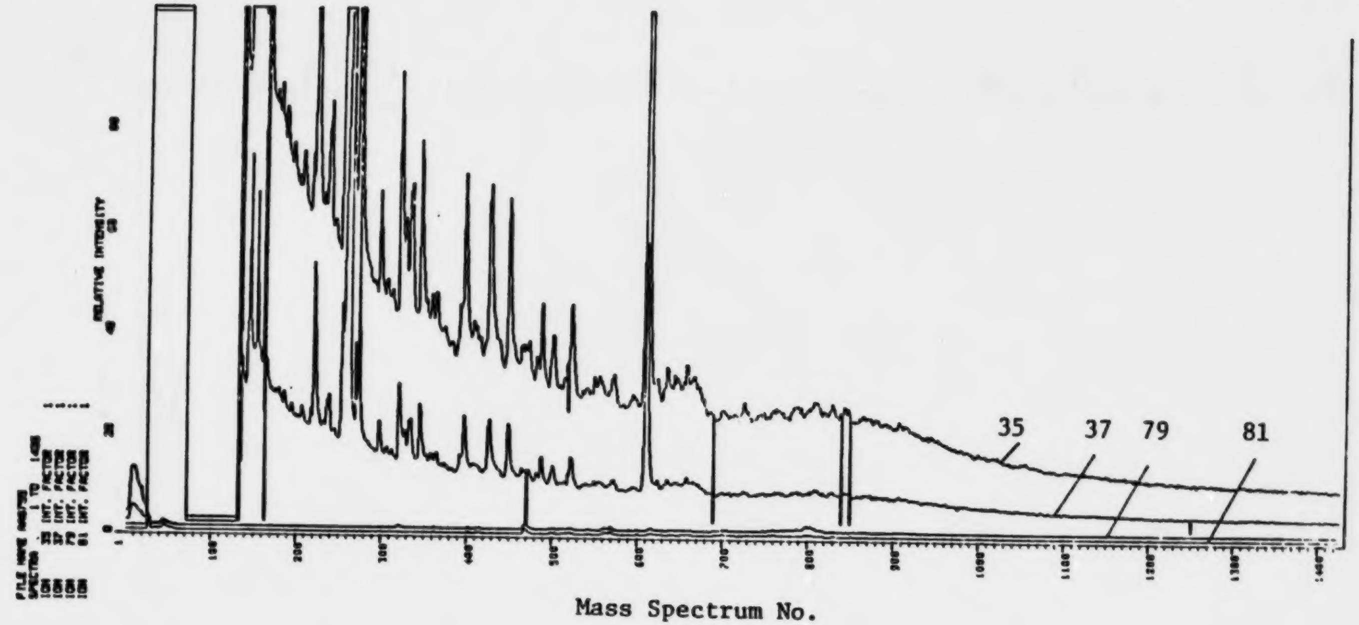

Figure A12. Negative chemical ionization GC/MS/COMP single ion profiles (m/z/ 35, 37, 79, 81) of "neutral" fraction for Effluent No. 1 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

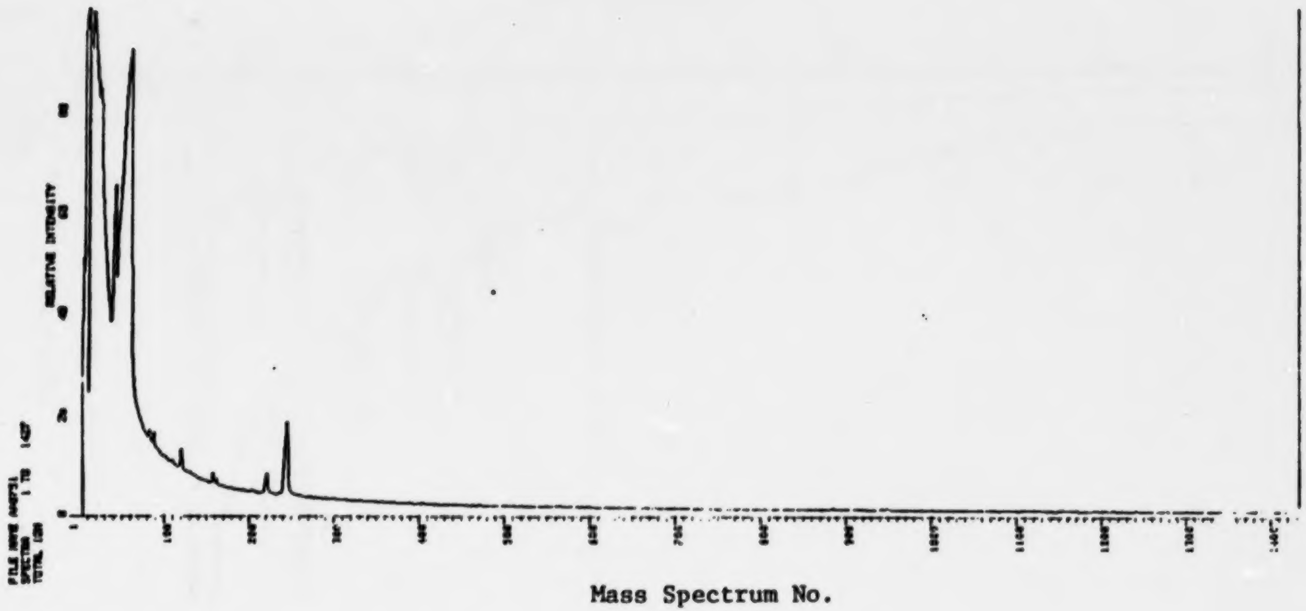

Figure A13. Electron impact GC/MS/COMP profile of "neutral" fraction for Effluent No. 2 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

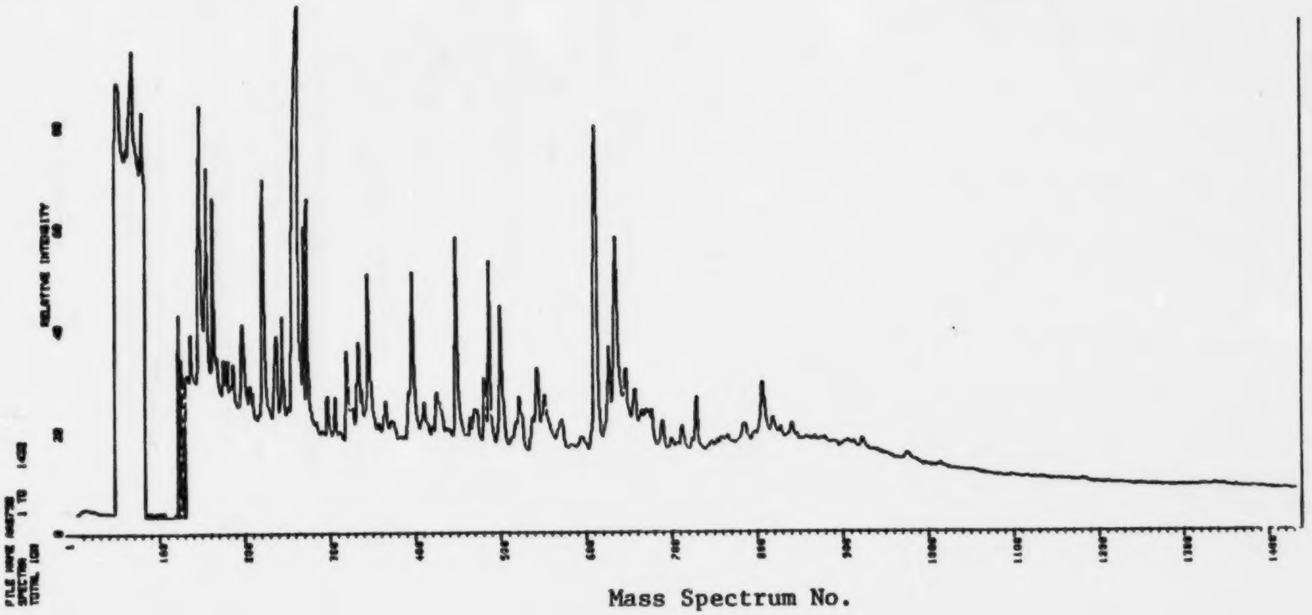

Figure A14. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction for Effluent No. 2 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m, fused silica capillary).

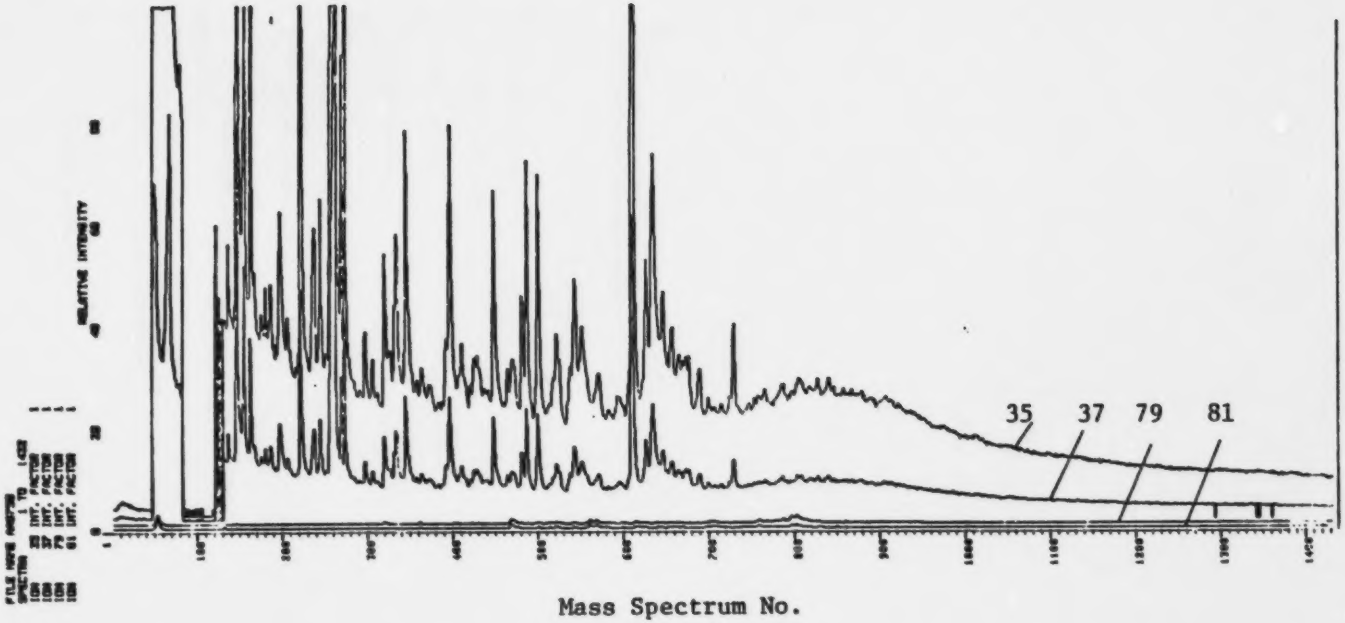

Figure A15. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "neutral" fraction for Effluent No. 2 from superchlorination process (SP2100, 0.23 mm x 25 m fused silica capillary).

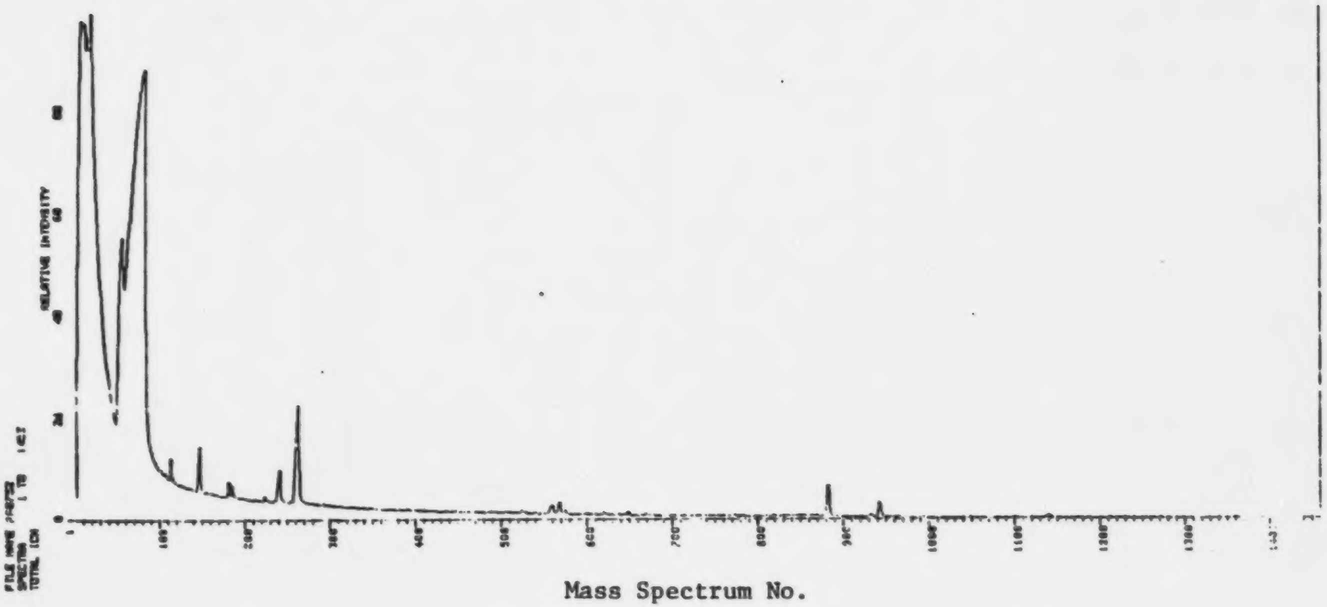

Figure A16. Electron impact GC/MS/COMP profile of "neutral" fraction for Effluent No. 3 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m, fused silica capillary).

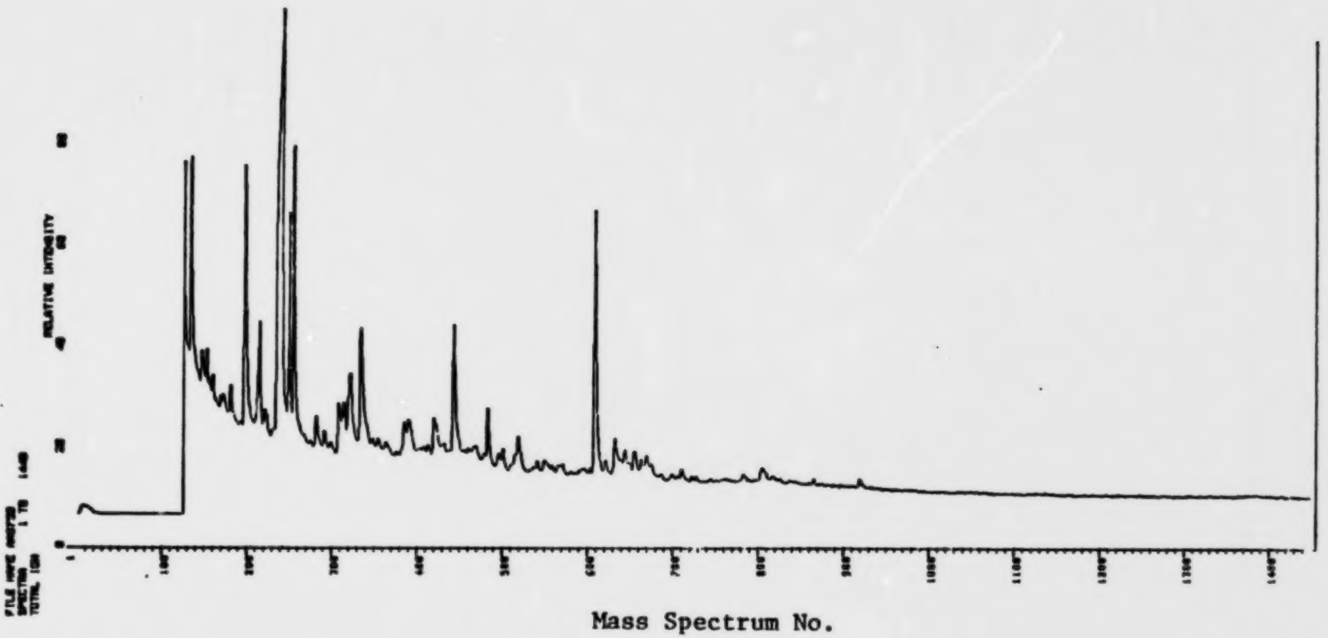

Figure A17. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction for Effluent No. 3 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m, fused silica capillary).

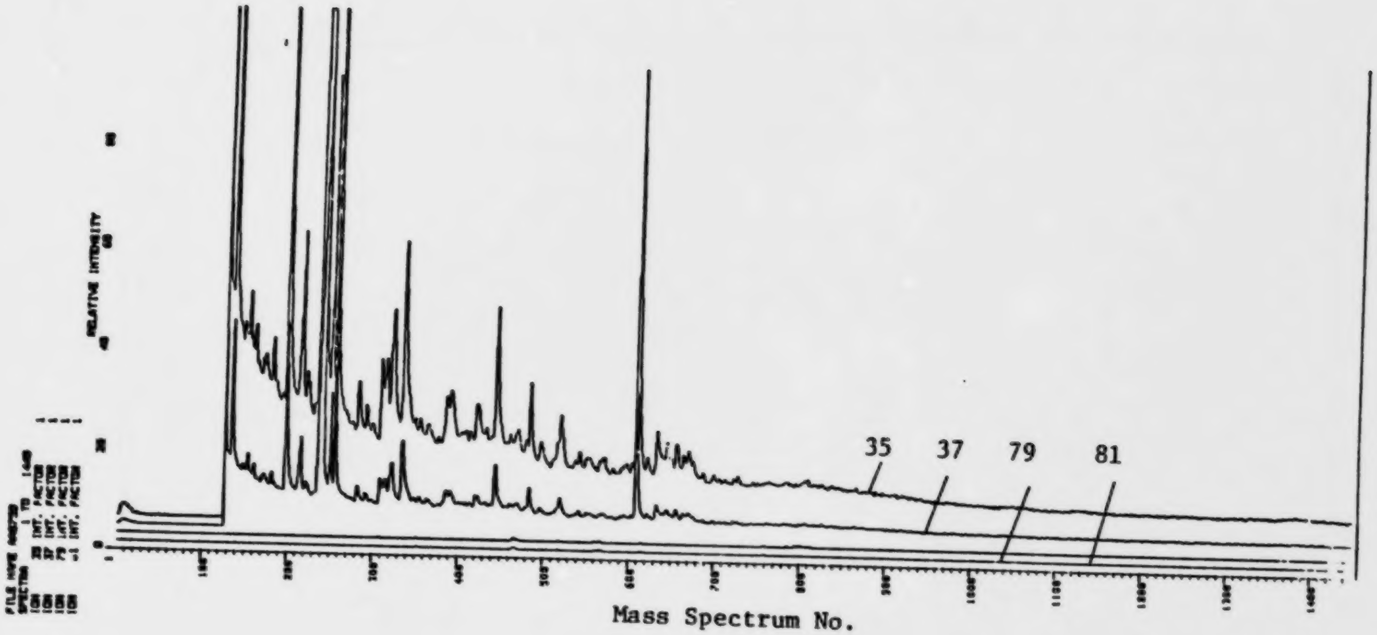

Figure A18. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "neutral" fraction for Effluent No. 3 from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

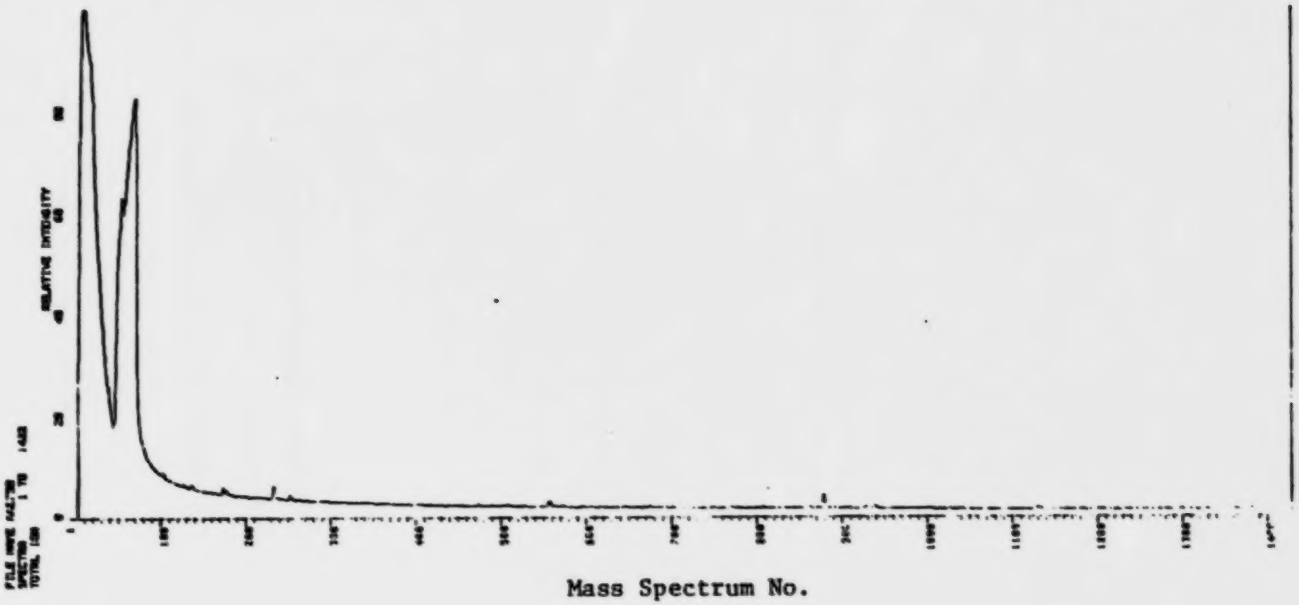

Figure A19. Electron impact GC/MS/COMP profile of "neutral" fraction for Settling Bed Sample from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

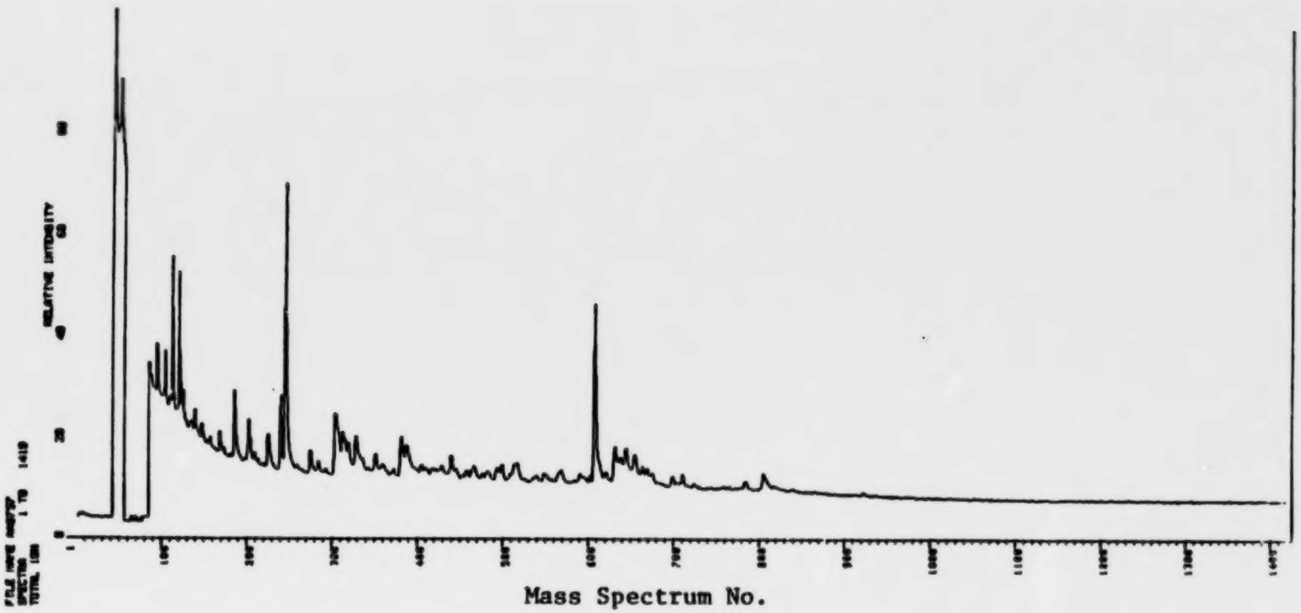

Figure A20. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction for Settling Bed Sample from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

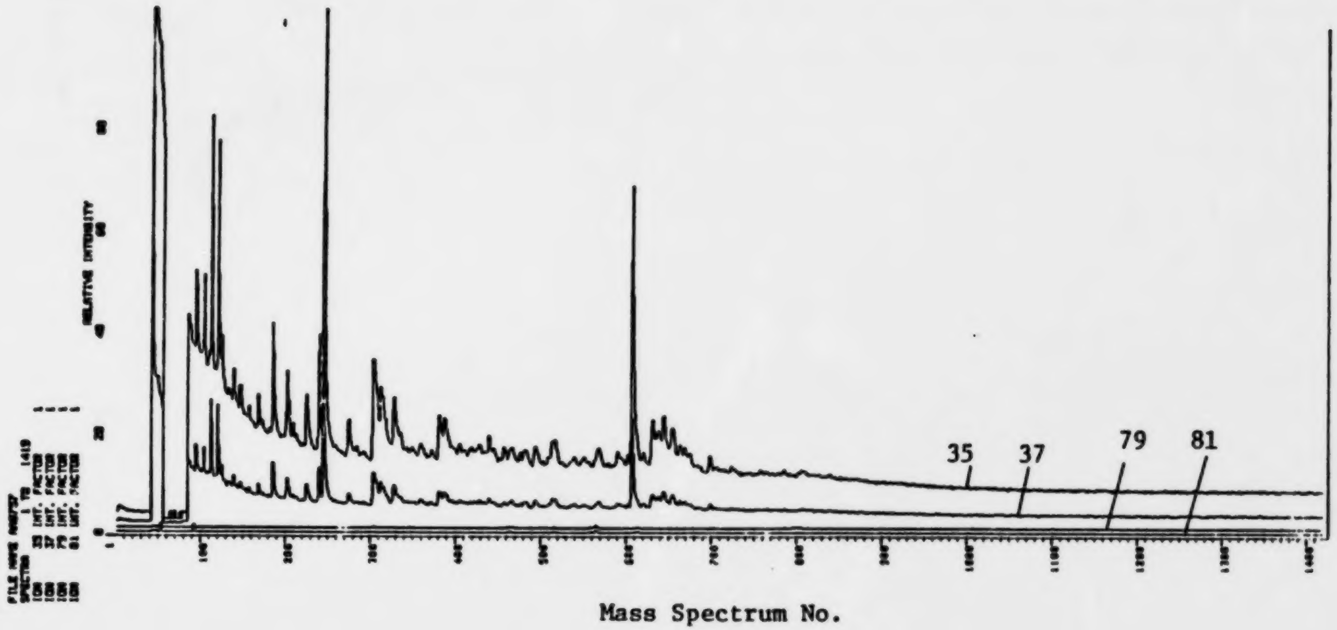

Figure A21. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "neutral" fraction for Settling Bed Sample from superchlorination process (SP2100, 0.23 mm i.d. x 25 m fused silica capillary).

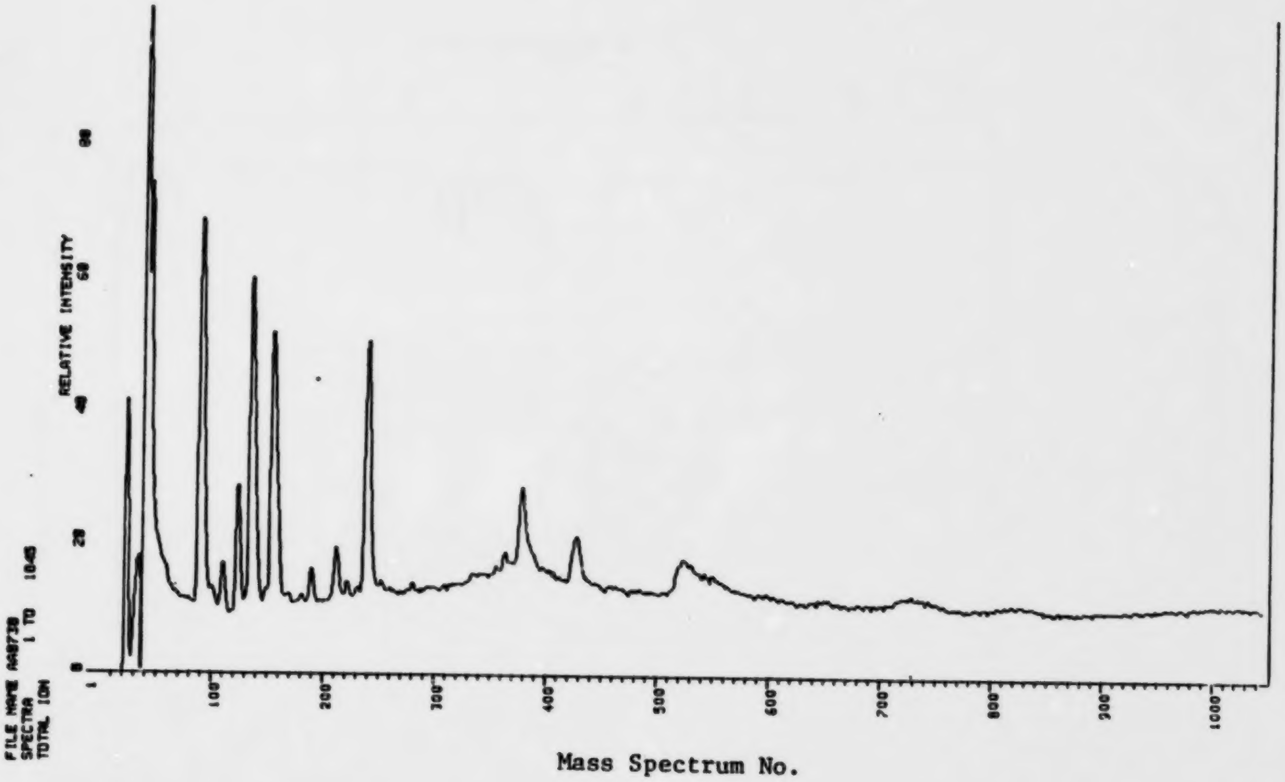

Figure A22. Electron impact GC/MS/COMP profile of "acid" fraction for Influent No. 1 from superchlorination process (SP1240 DA packed column).

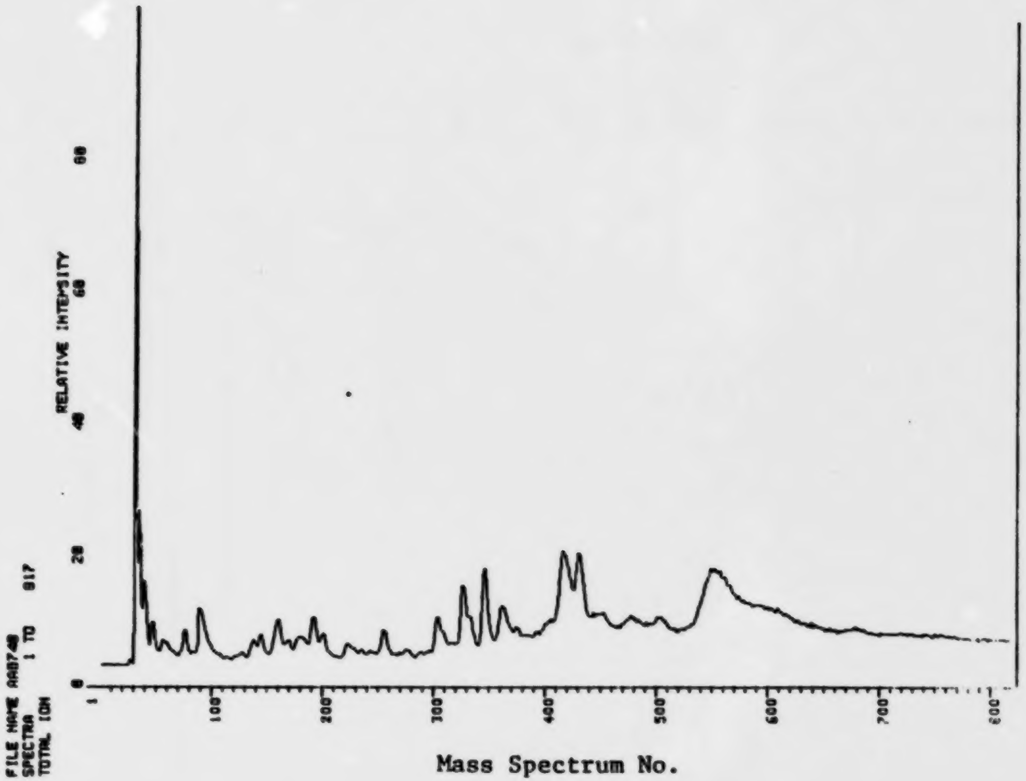

Figure A23. Negative chemical ionization GC/MS/COMP profile of "acid" fraction for Influent No. 1 from superchlorination process (SP1240 DA packed column).

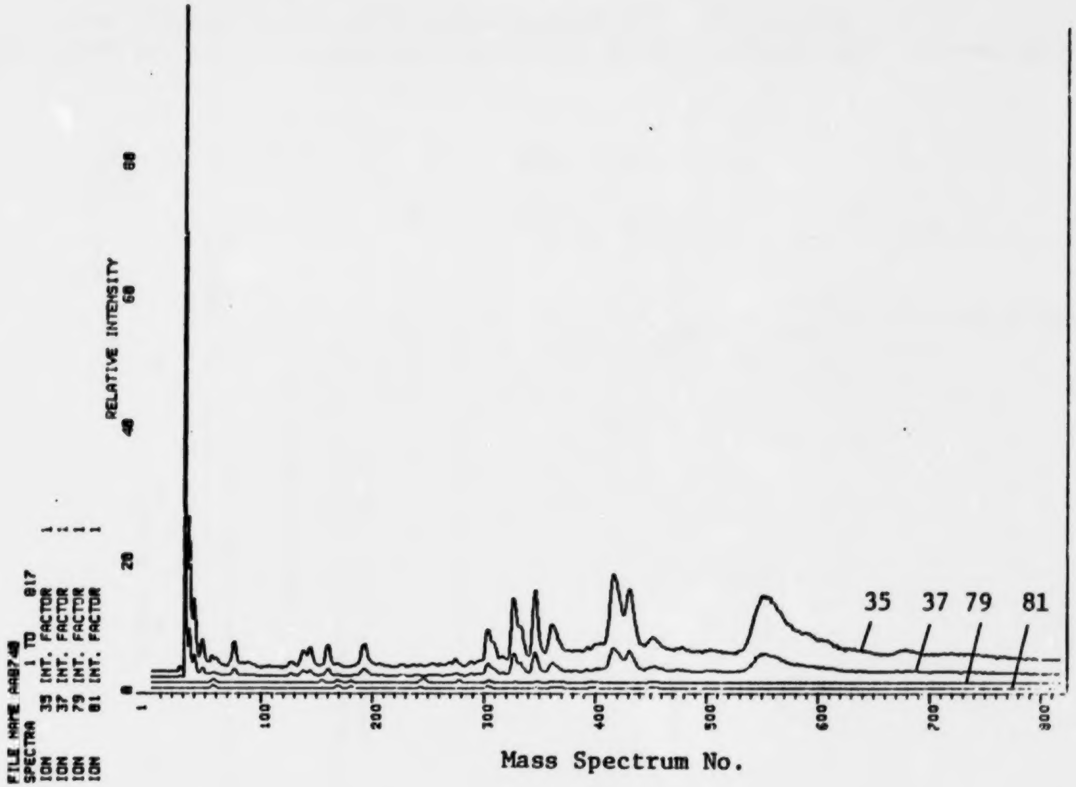

Figure A24. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "acid" fraction for Influent No. 1 from superchlorination process (SP1240 DA packed column).

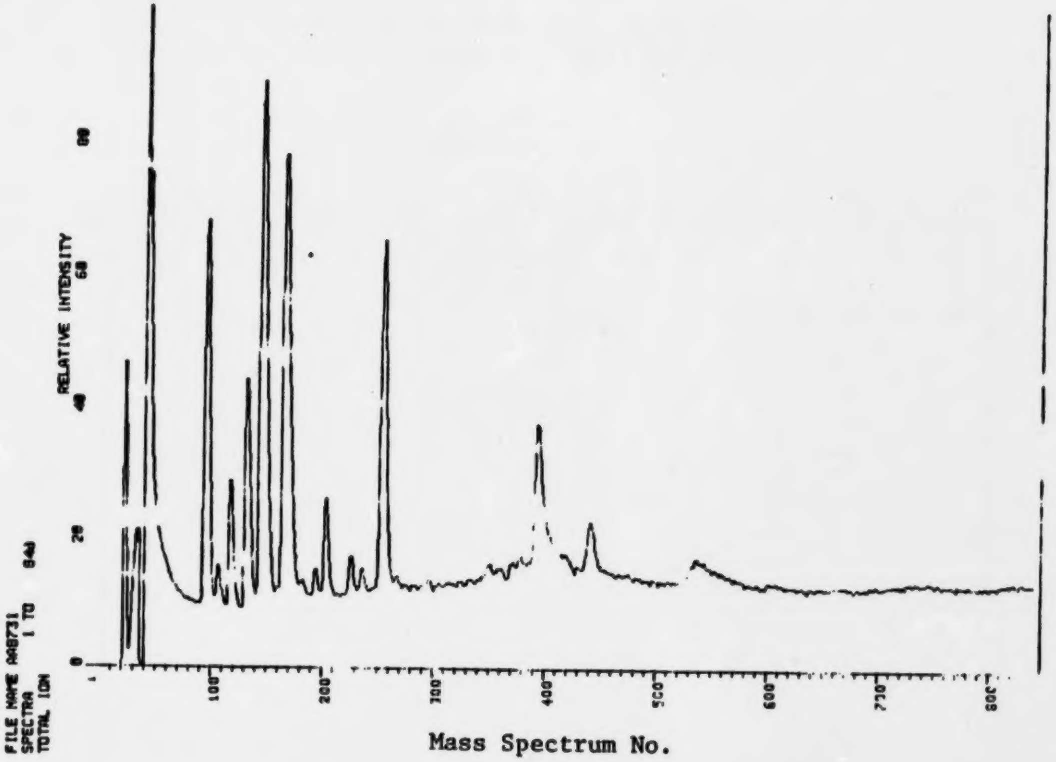

Figure A25. Electron impact GC/MS/COMP profile of "acid" fraction for Influent No. 2 from superchlorination process (SP1240 DA packed column).

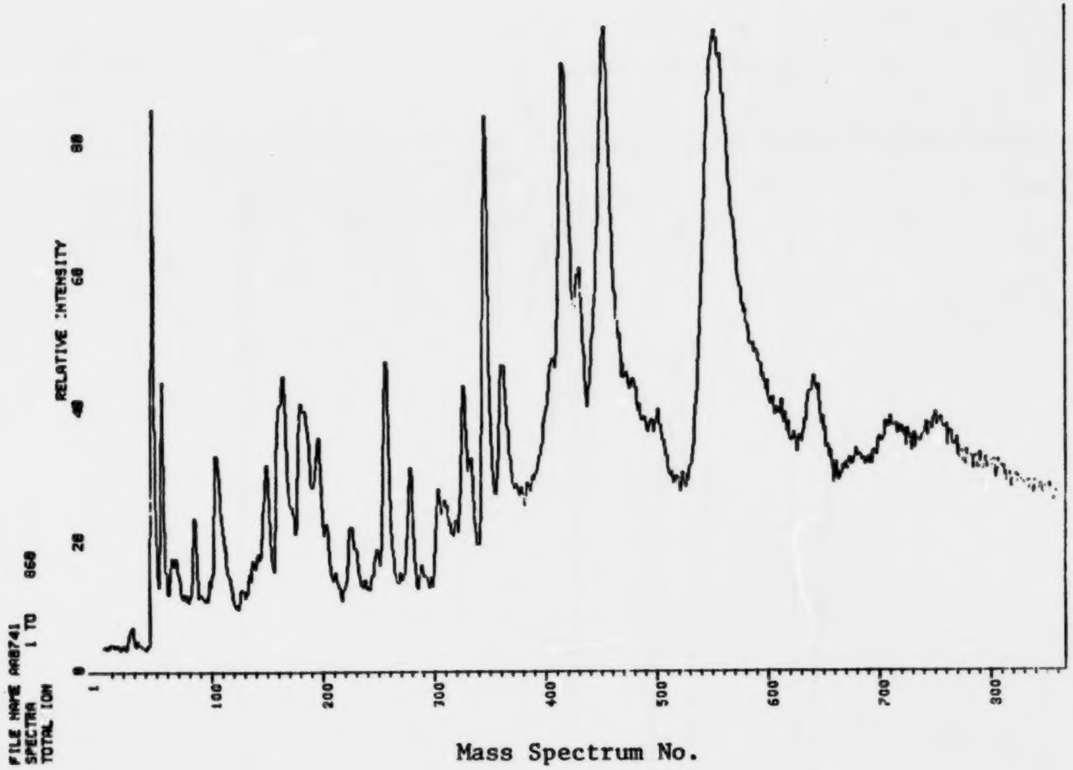

Figure A26. Negative chemical ionization GC/MS/COMP profile of "acid" fraction from Influent No. 2 for superchlorination process (SP1240 DA packed column).

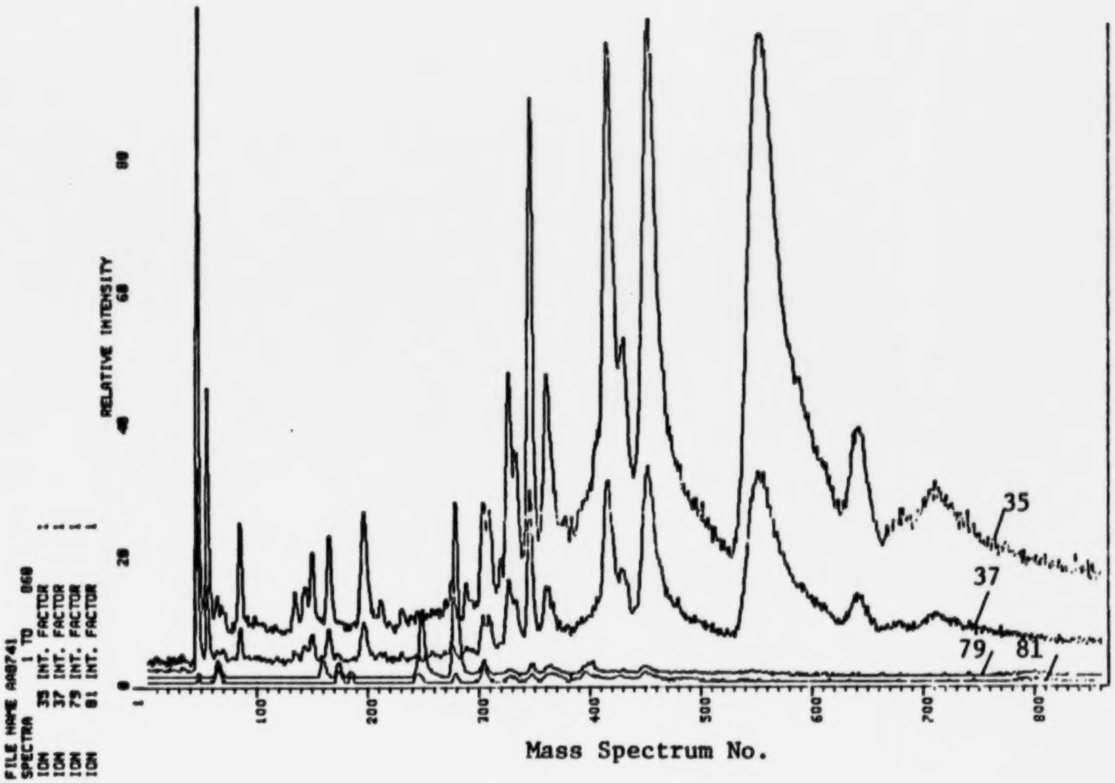

Figure A27. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "acid" fraction for Influent No. 2 from superchlorination process (SP1240 DA packed column).

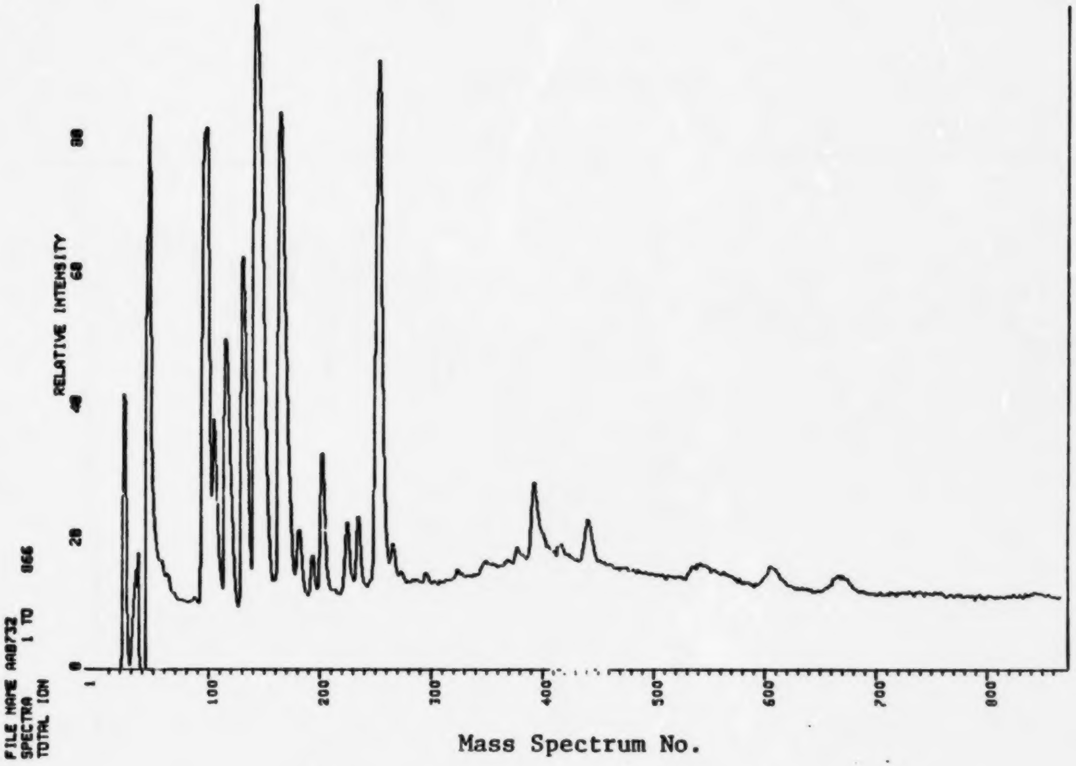

Figure A28. Electron impact GC/MS/COMP profile of "acid" fraction for Influent No. 3 from superchlorination process (SP1240 DA packed column).

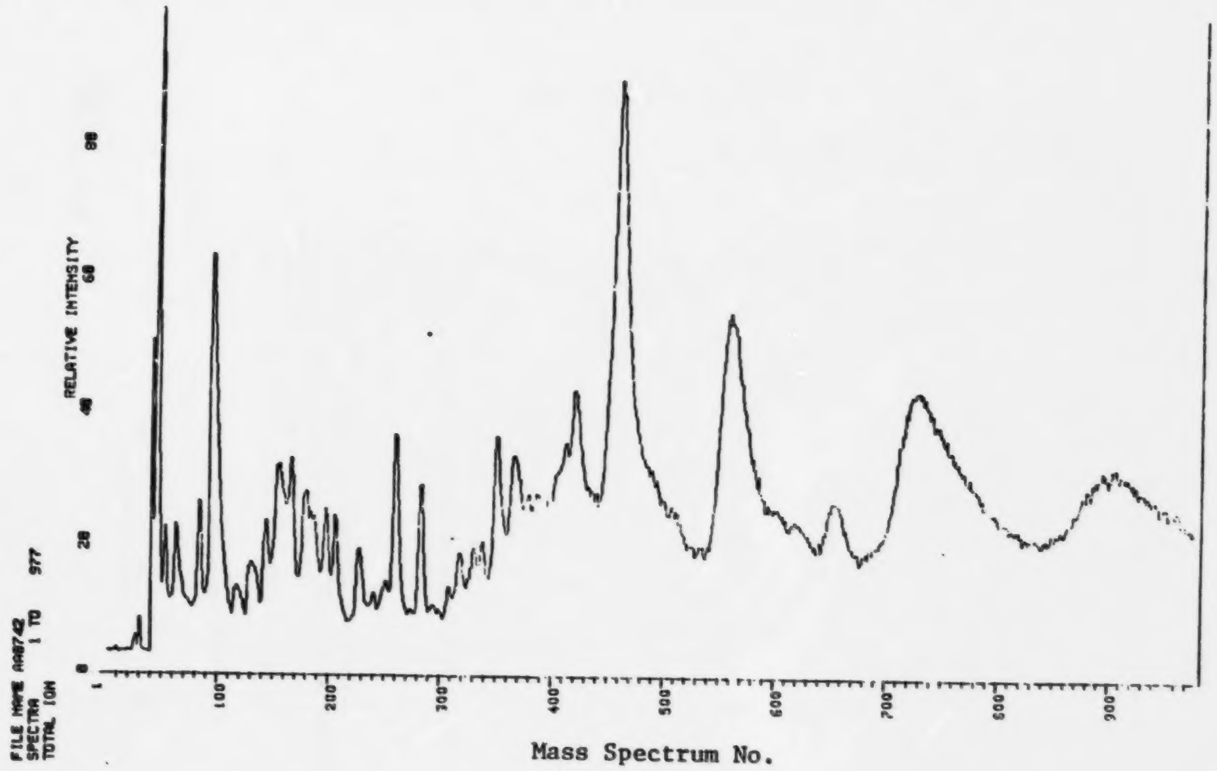

Figure A29. Negative chemical ionization GC/MS/COMP profile of "acid" fraction for Influent No. 3 from superchlorination process (SP1240 DA packed column).

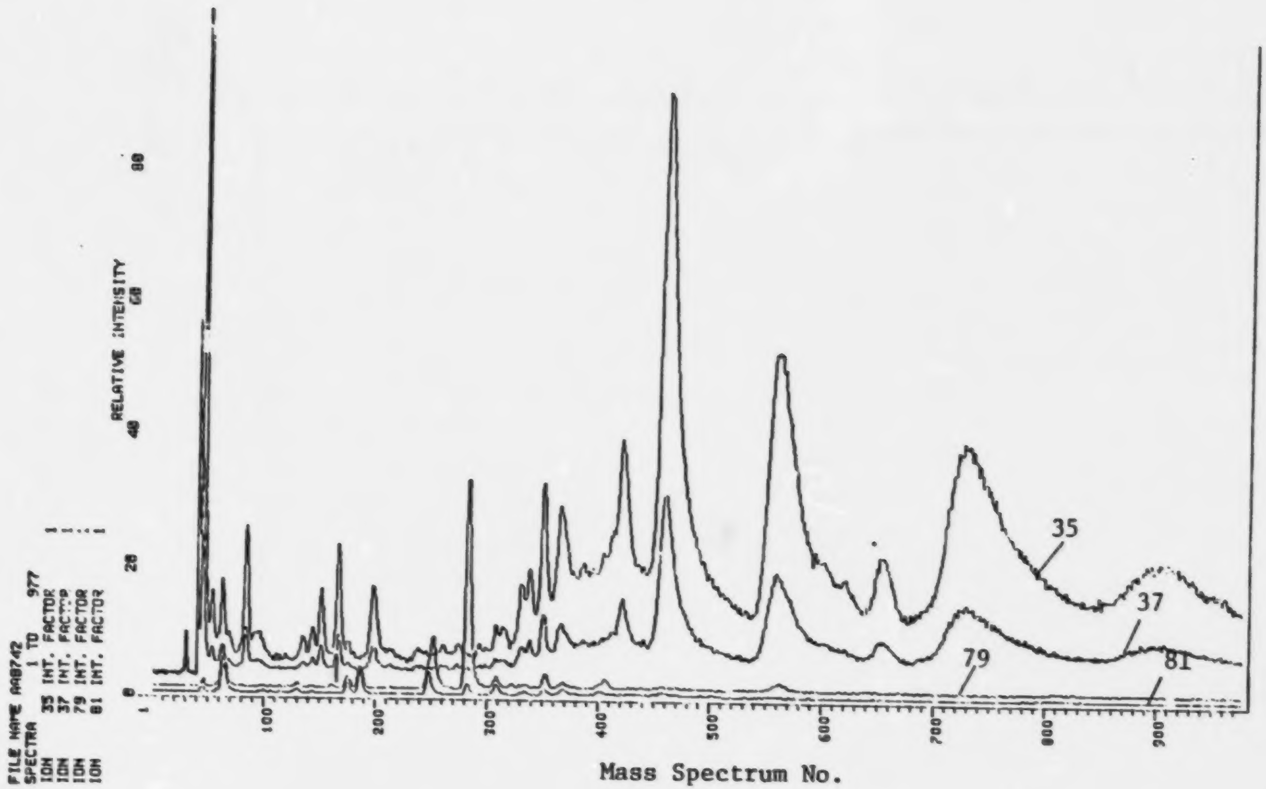

Figure A30. Negative chemical ionization GC/MS/COMP single ion profiles of "acid" fraction for Influent No. 3 for superchlorination process (SP1240 DA packed column).

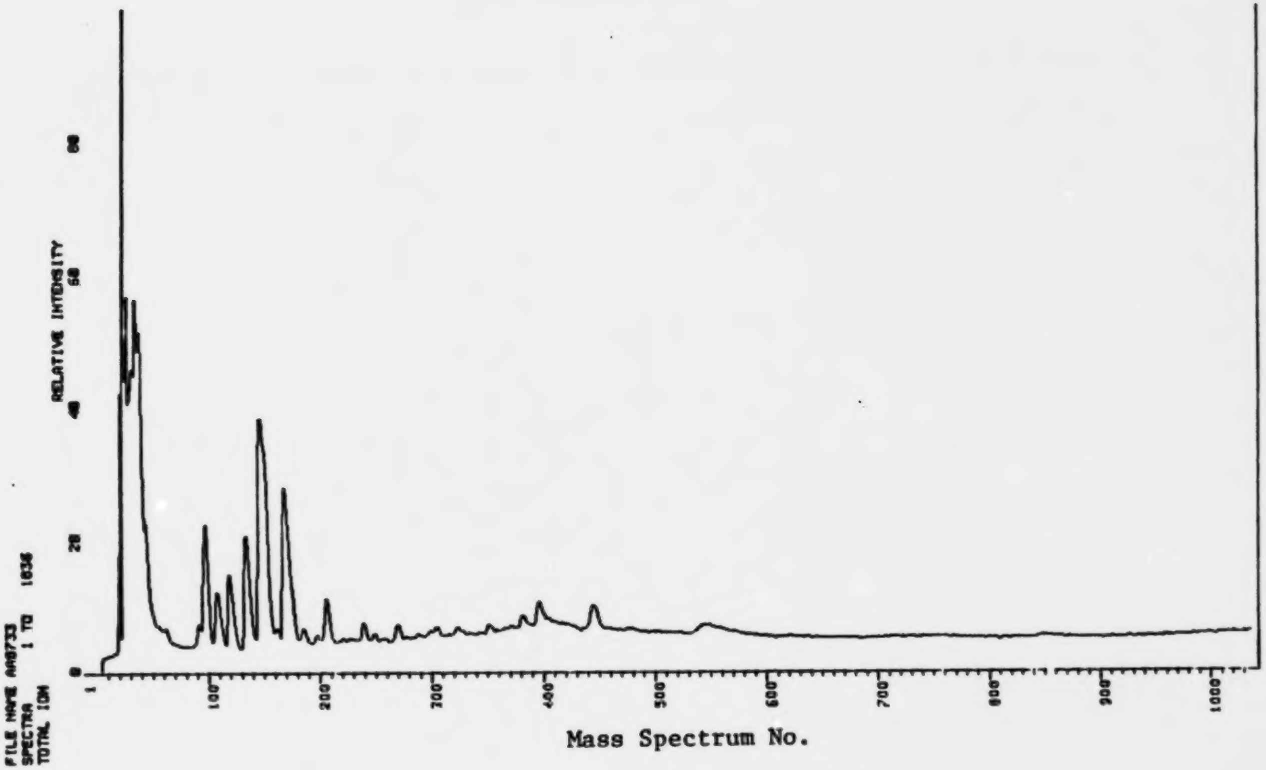

Figure A31. Electron impact GC/MS/COMP profile of "acid" fraction for Effluent No. 1 from superchlorination process (SP1240 DA packed column).

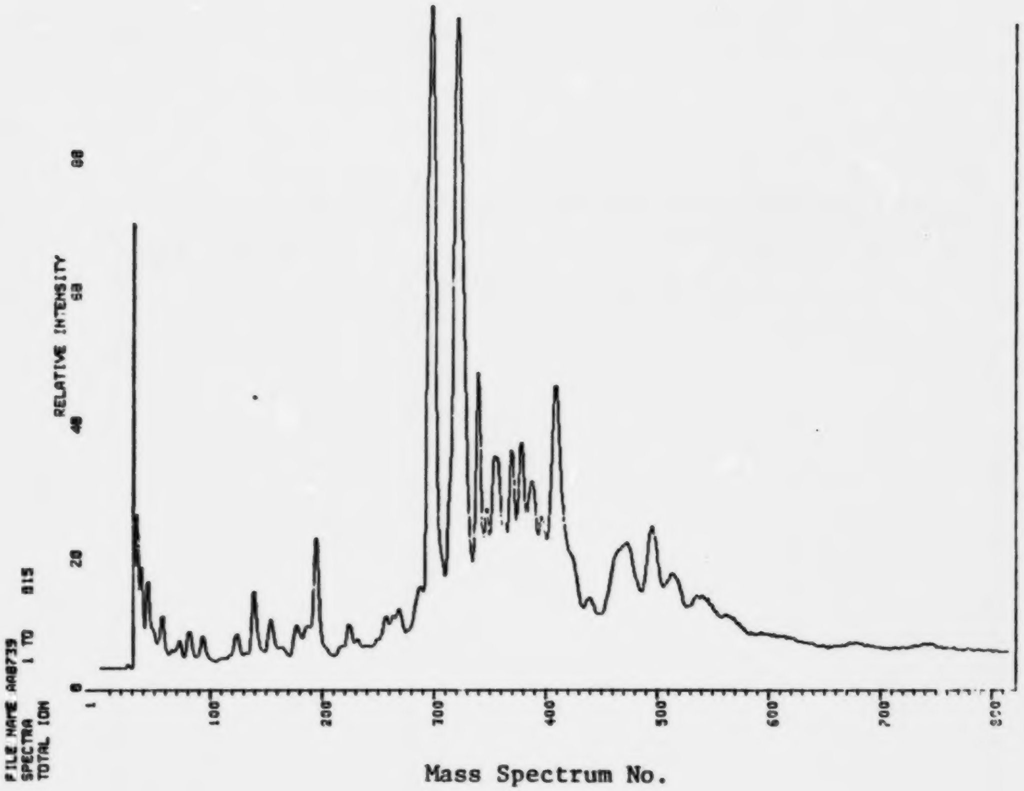

Figure A32. Negative chemical ionization GC/MS/COMP profile of "acid" fractio for Effluent No. 1 from superchlorination process (SP1240 DA packed column).

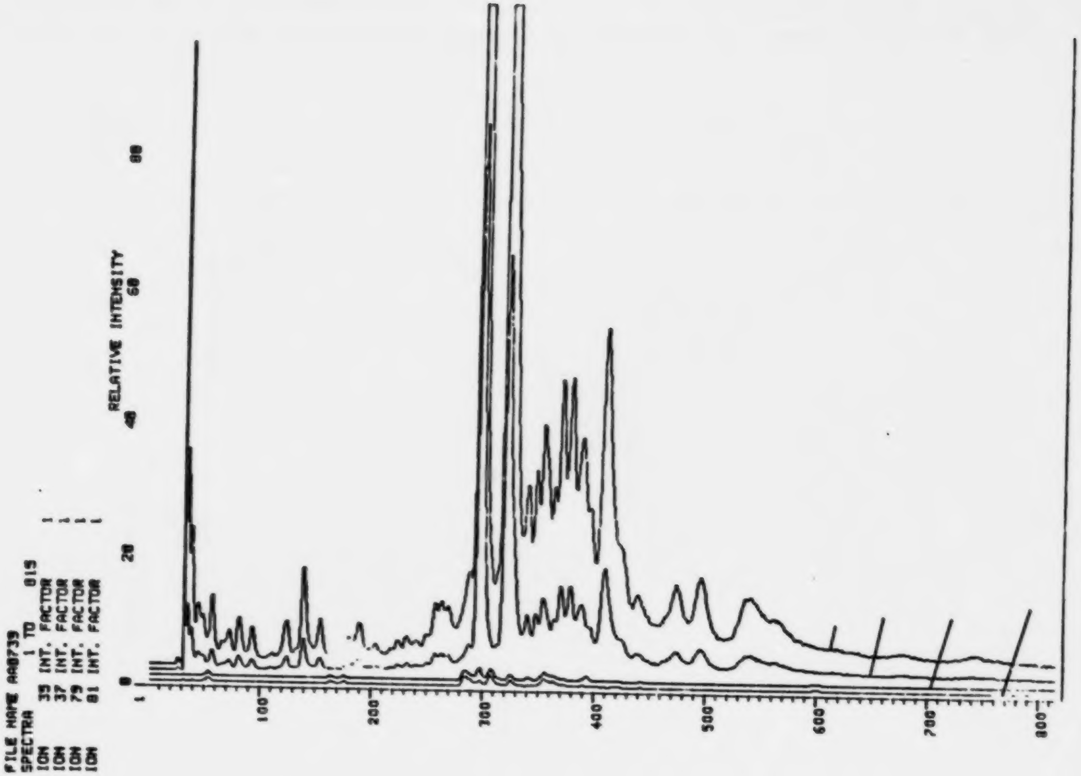

Figure A33. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "acid" fraction for Effluent No. 1 from superchlorination process (SP1240 DA packed column).

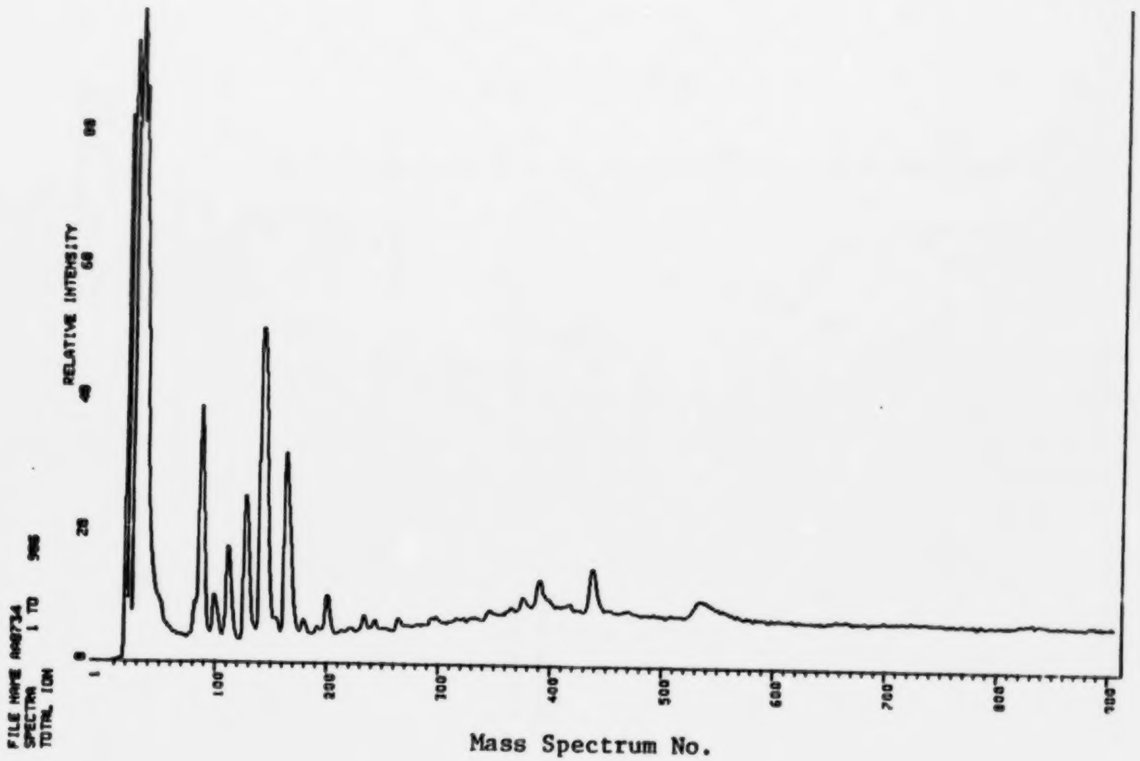

Figure A34. Electron impact GC/MS/COMP profile of "acid" fraction for Effluent No. 2 from superchlorination process (SP1240 DA packed column).

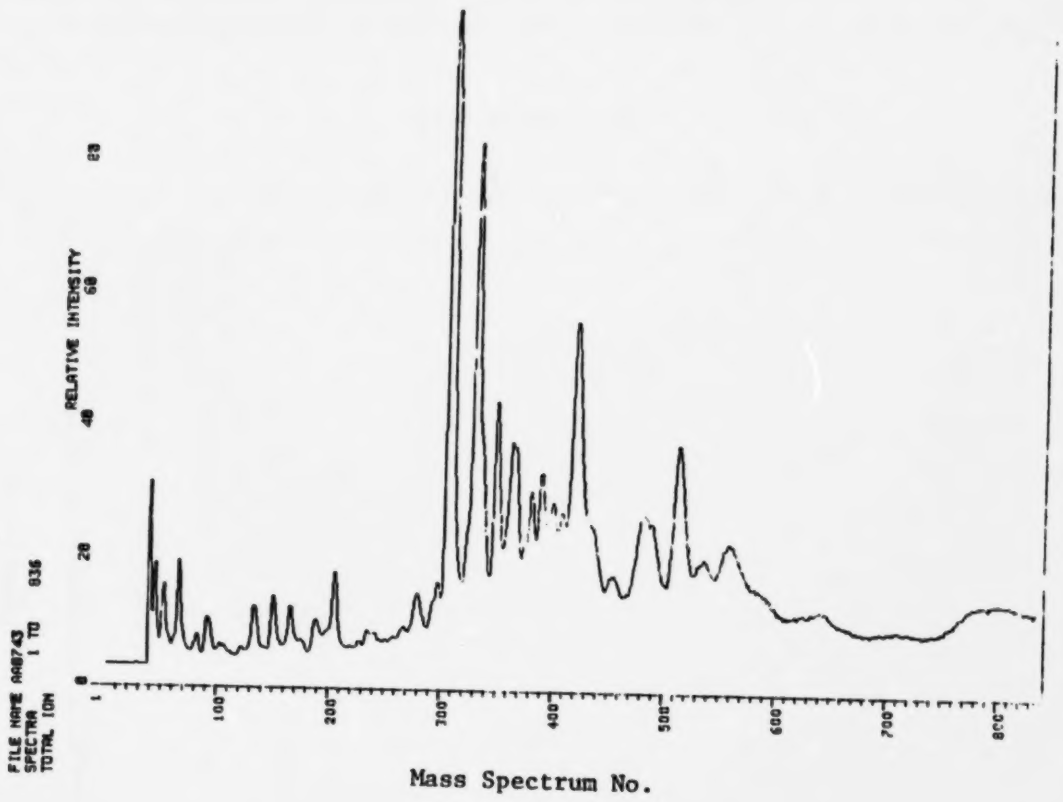

Figure A35. Negative chemical ionization GC/MS/COMP profile of "acid" fraction for Effluent No. 2 from superchlorination process (SP1240 DA packed column).

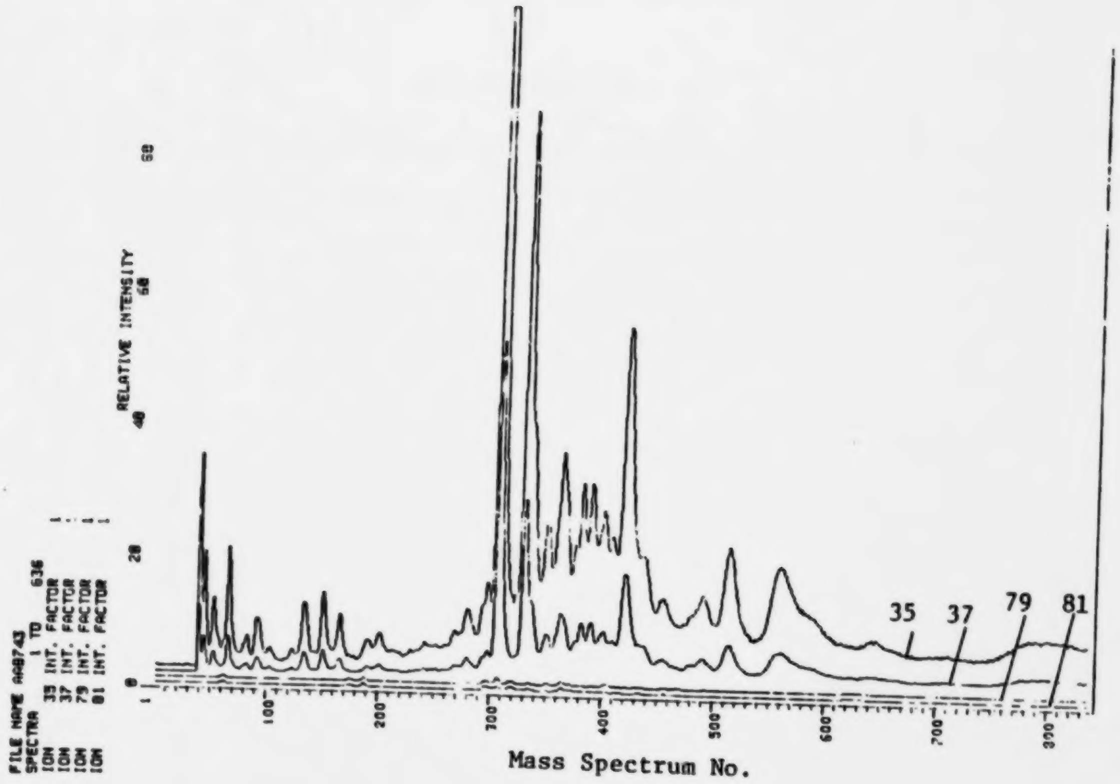

Figure A36. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "acid" fraction for Effluent No. 2 from superchlorination process (SP1240 DA packed column).

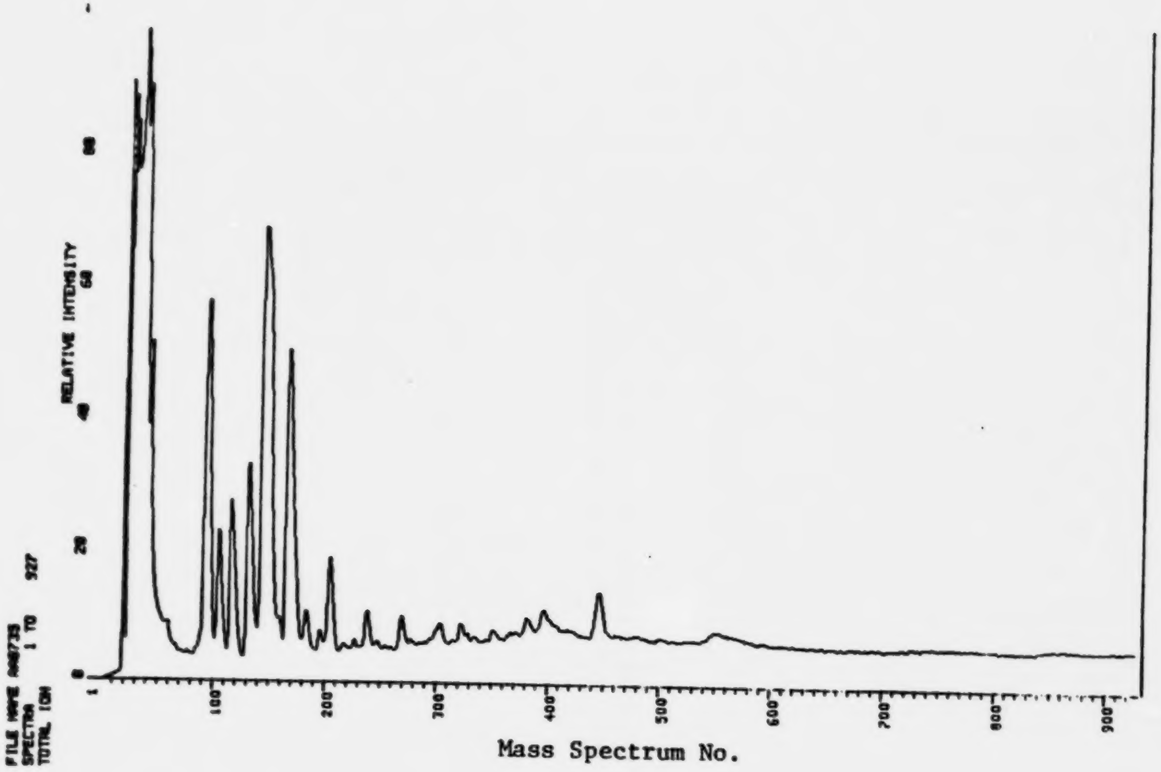

Figure A37. Electron impact GC/MS/COMP profile of "acid" fraction for Effluent No. 3 from superchlorination process (SP1240 DA packed column).

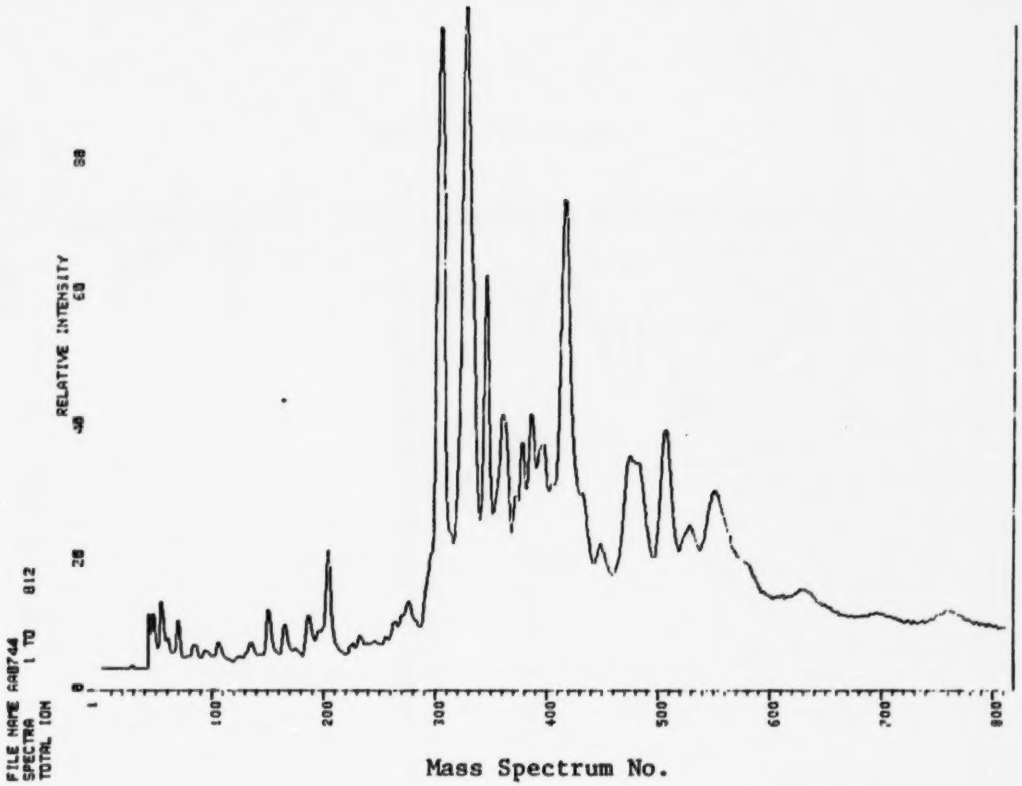

Figure A38. Negative chemical ionization GC/MS/COMP profile of "acid" fraction from Effluent No. 3 from superchlorination process (SP1240 DA packed column).

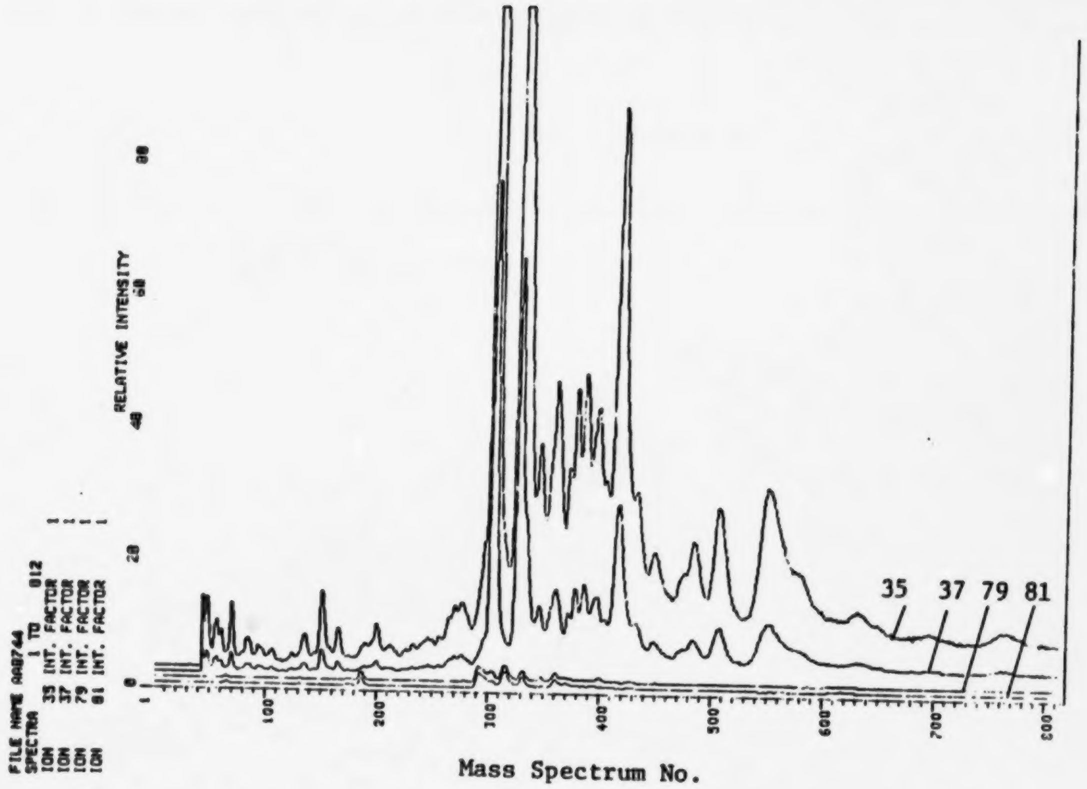

Figure A39. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "acid" fraction for Effluent No. 3 from superchlorination process (SP1240 DA packed column).

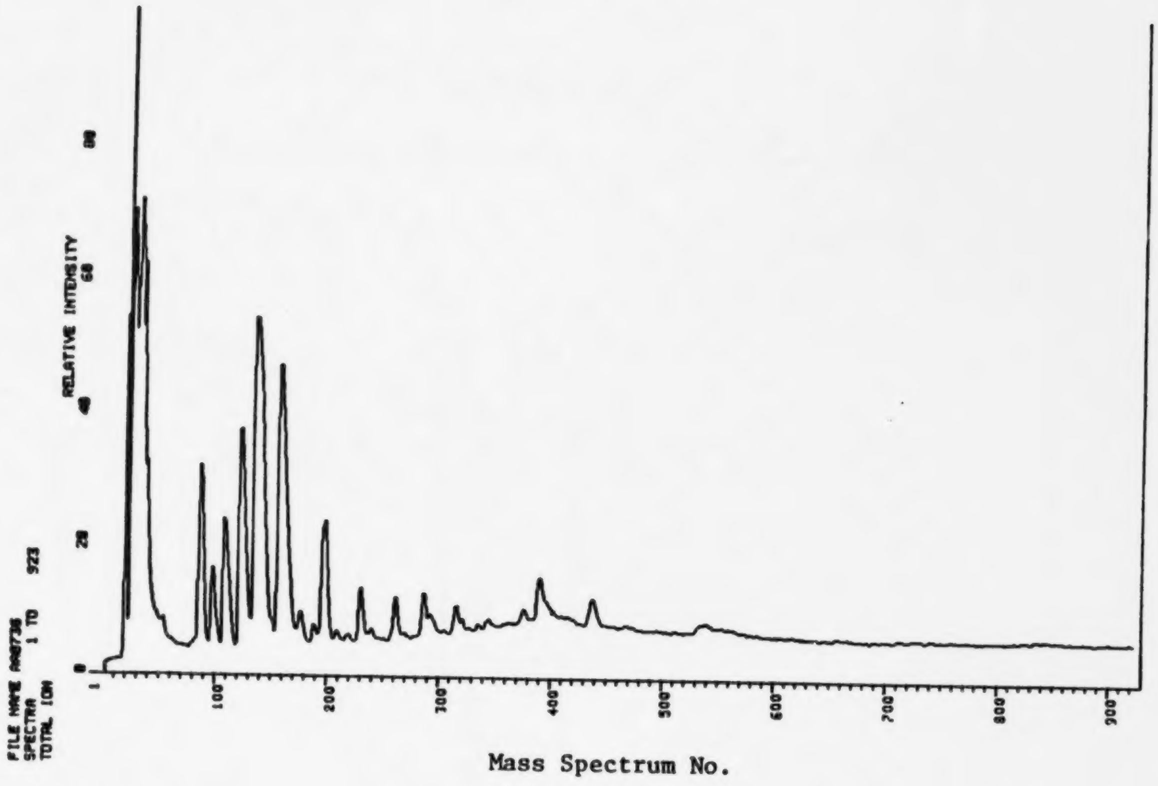

Figure A40. Electron impact GC/MS/COMP profile of "acid" fraction for Settling Bed Sample from superchlorination process (SP1240 DA packed column).

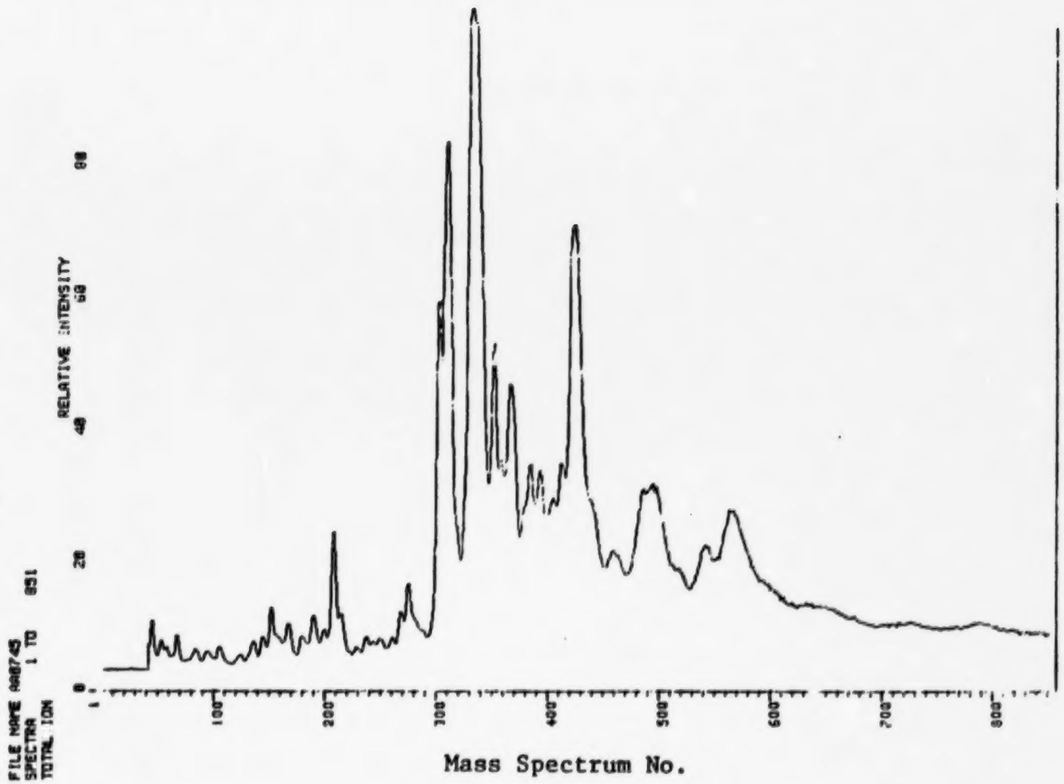

Figure A41. Negative chemical ionization GC/MS/COMP profile of "acid" fraction from Settling Bed Sample for superchlorination process (SP1240 DA packed column).

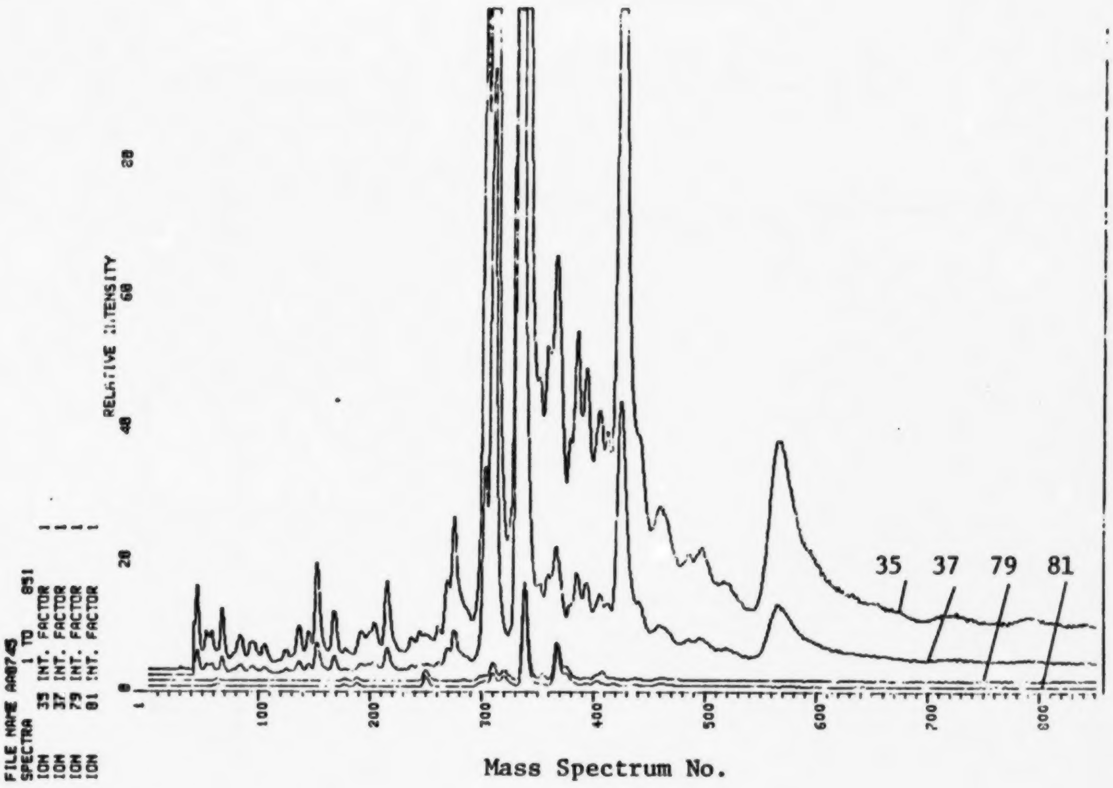

Figure A42. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "acid" fraction for Settling Bed Sample from superchlorination process (SP1240 DA packed column).

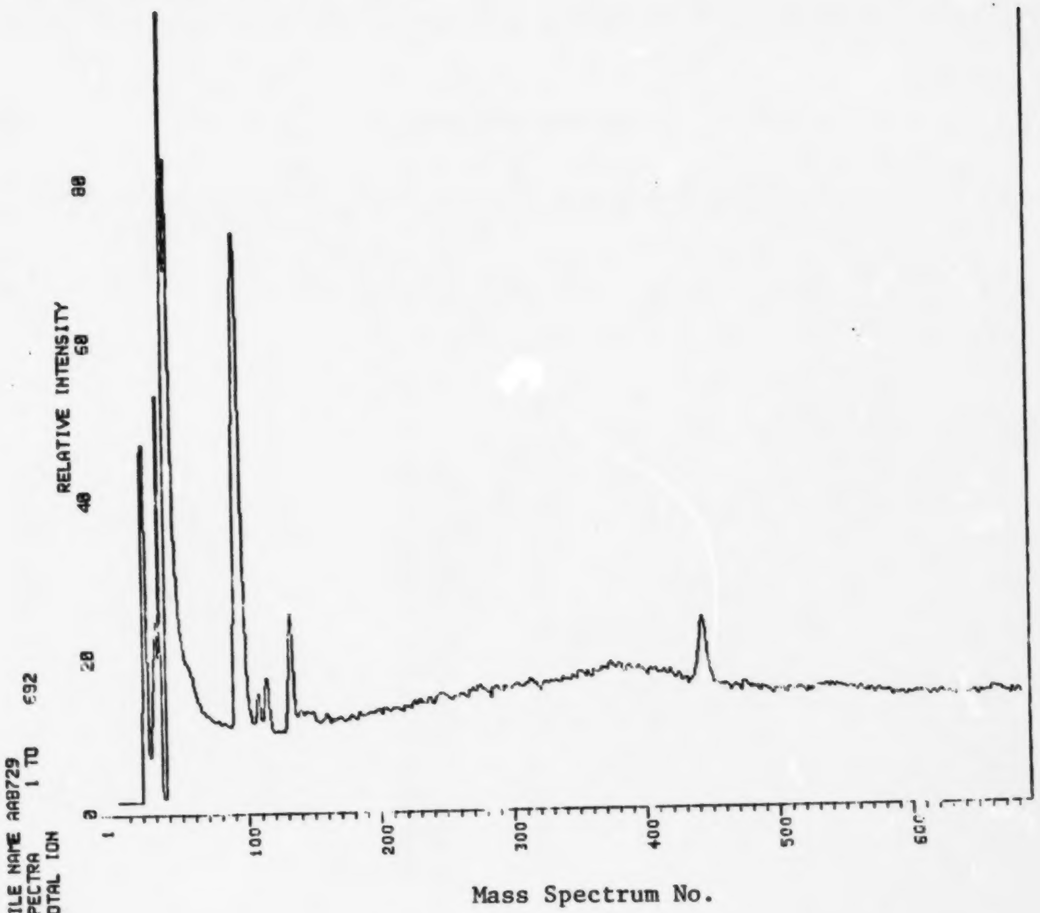

Figure A43 . Electron impact GC/MS/COMP profile of "acid" solvent blank (SP1240 DA packed column).

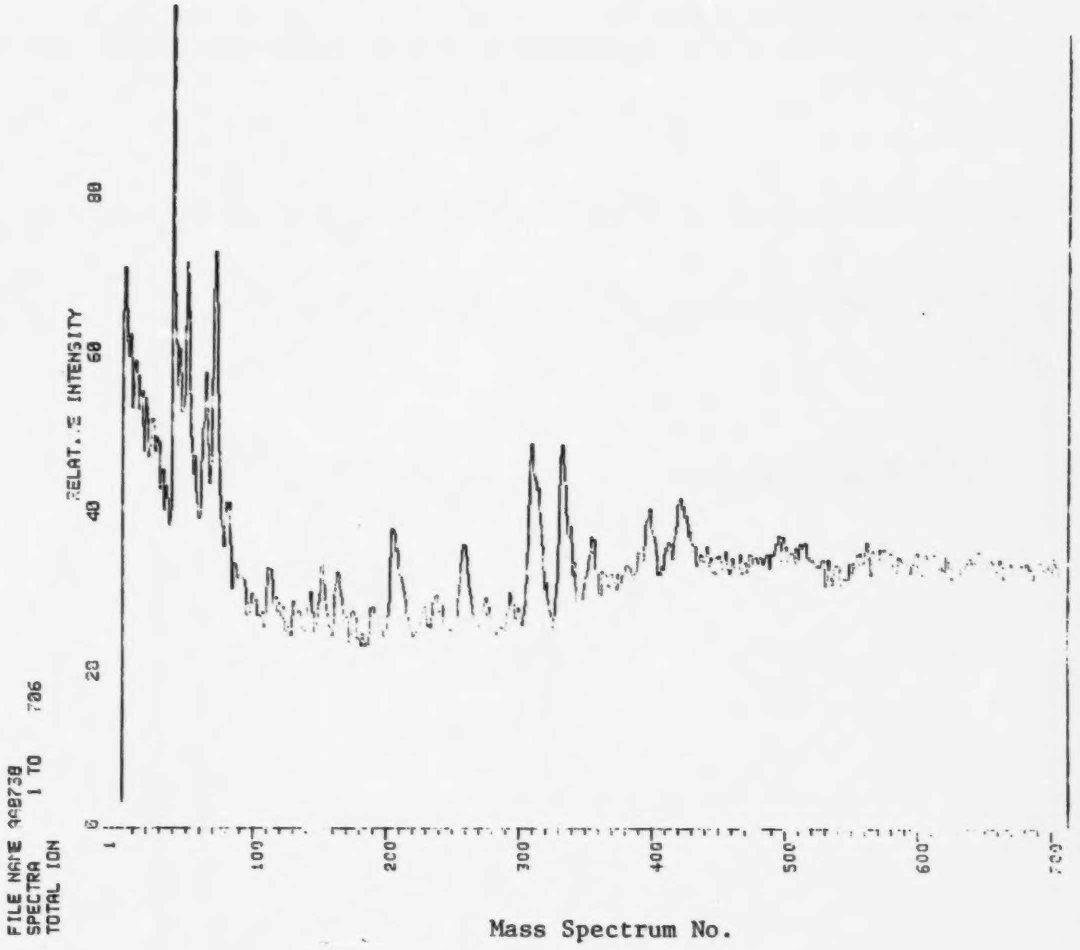

Figure A44. Negative chemical ionization GC/MS/COMP profile of "acid" solvent blank (SP2100 packed column).

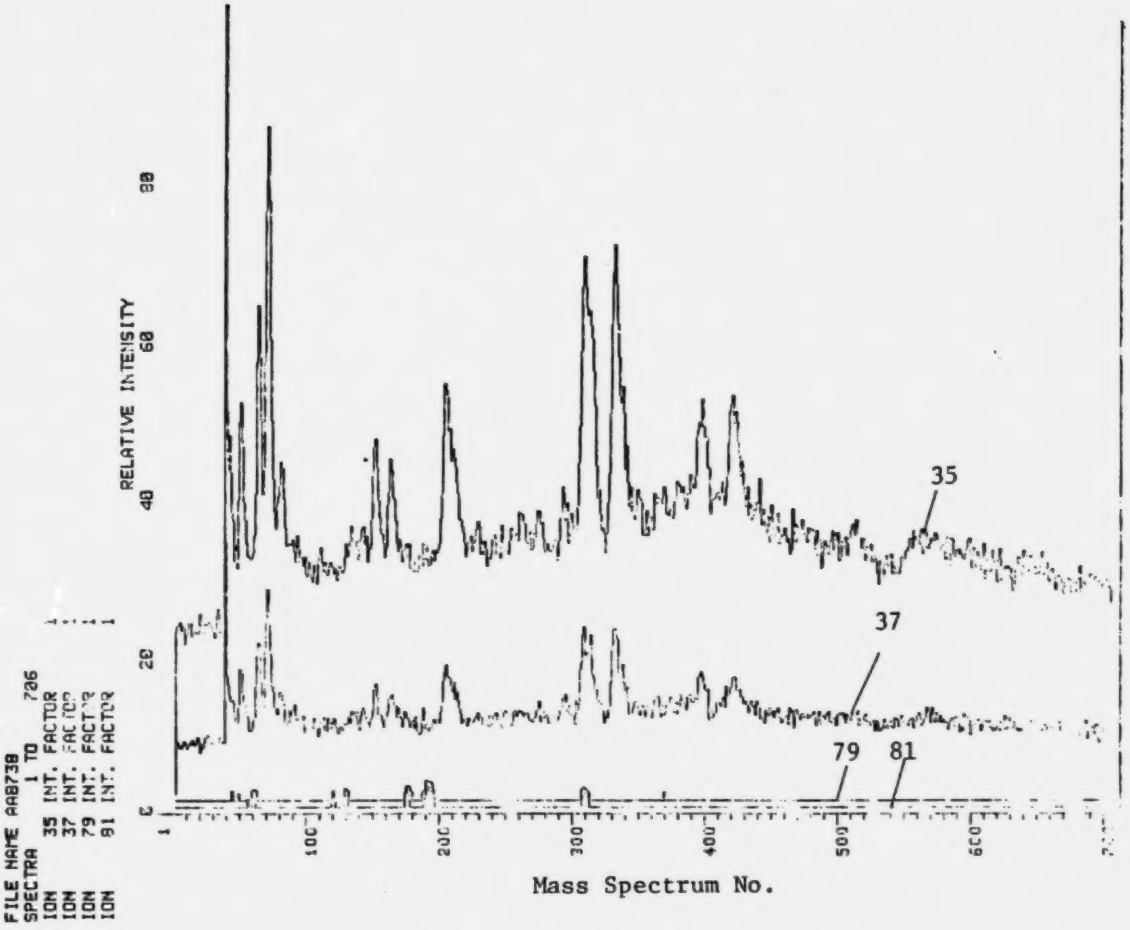

Figure A45. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "acid" solvent blank (SP1240 DA packed column).

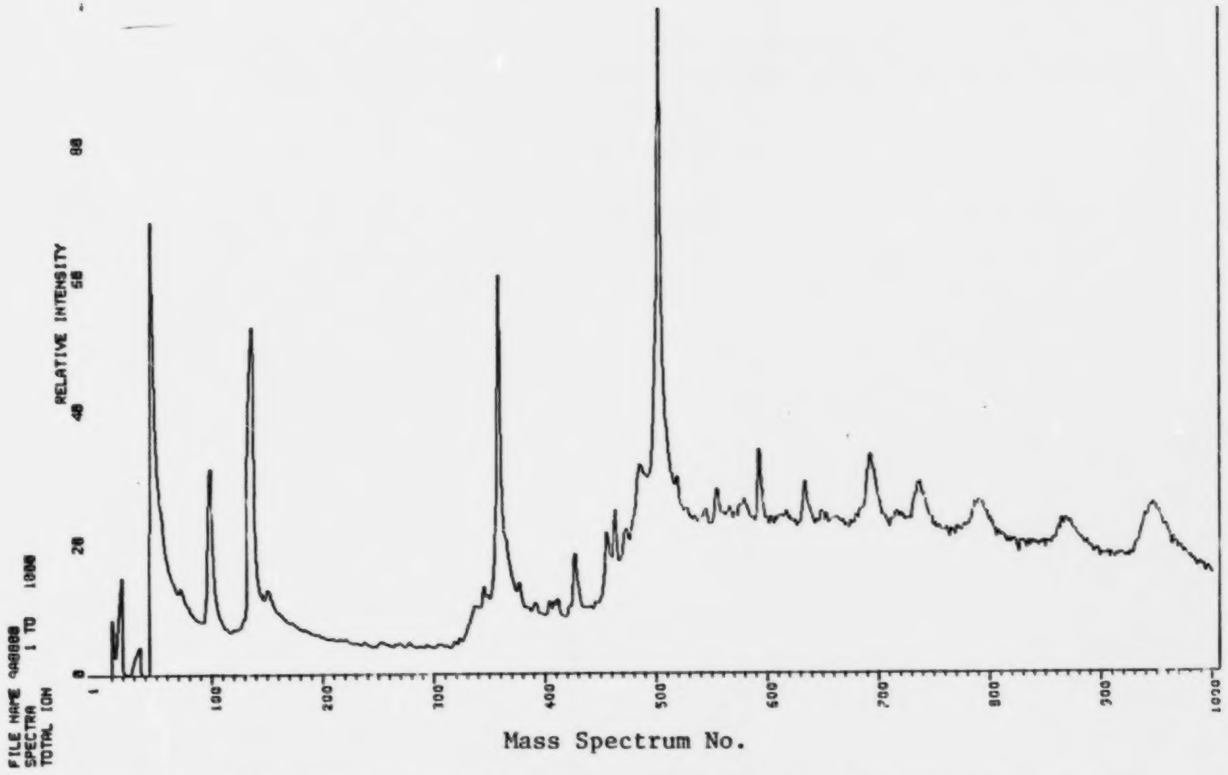

Figure A46. Electron impact GC/MS/COMP profile of GP1 "neutral" fraction for Influent No. 2 (SP2100 capillary).

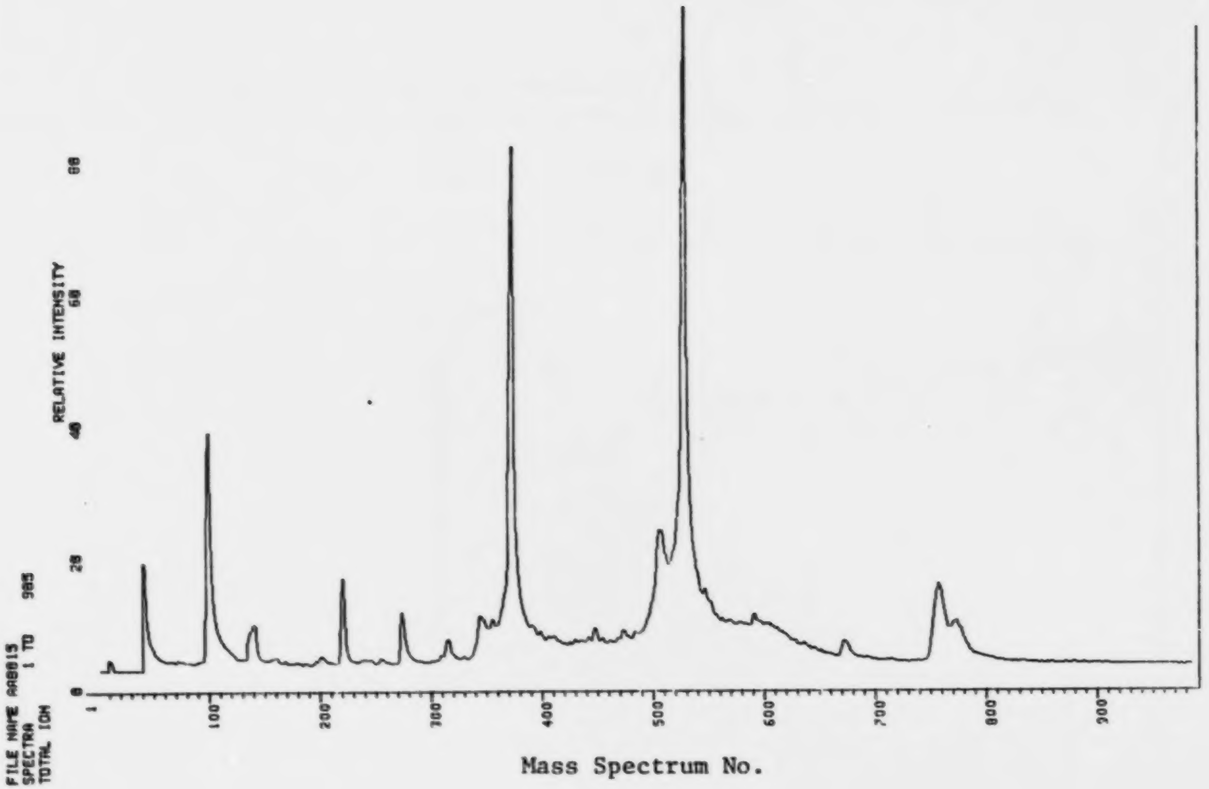

Figure A47. Negative chemical ionization GC/MS/COMP profile of GP1 "neutral fraction for Influent No. 2 (SP2100 capillary).

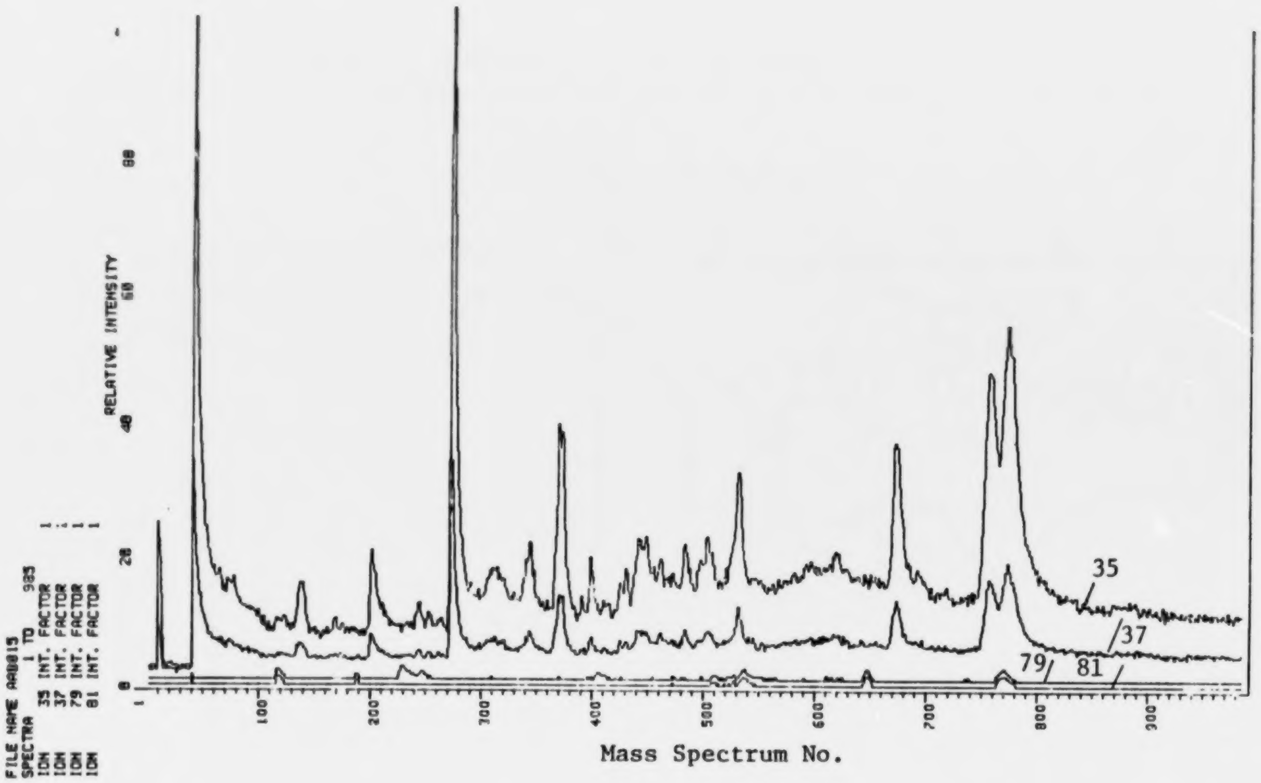

Figure A48. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GP1 "neutral" fraction for Influent No. 2 (SP2100 capillary).

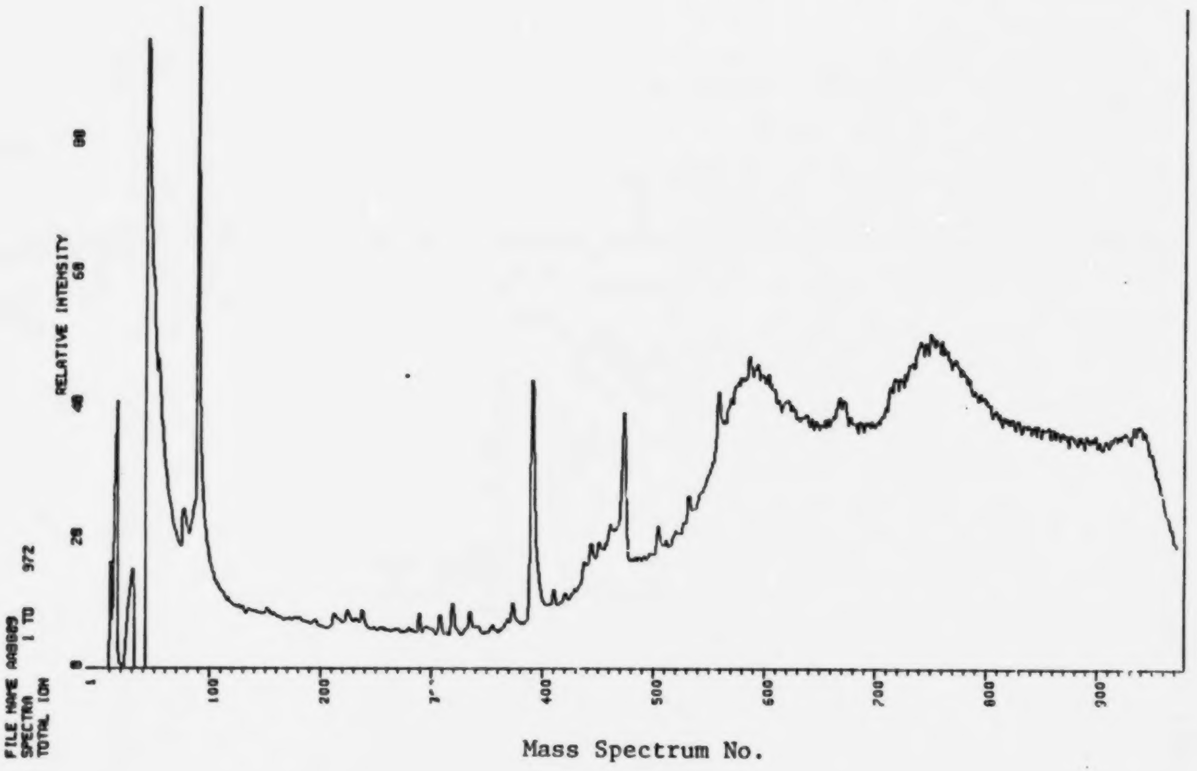

Figure A49. Electron impact GC/MS/COMP profile of GP4 "neutral" fraction for Influent No. 2 sample (SP2100 capillary).

GP4 NeuT INF2

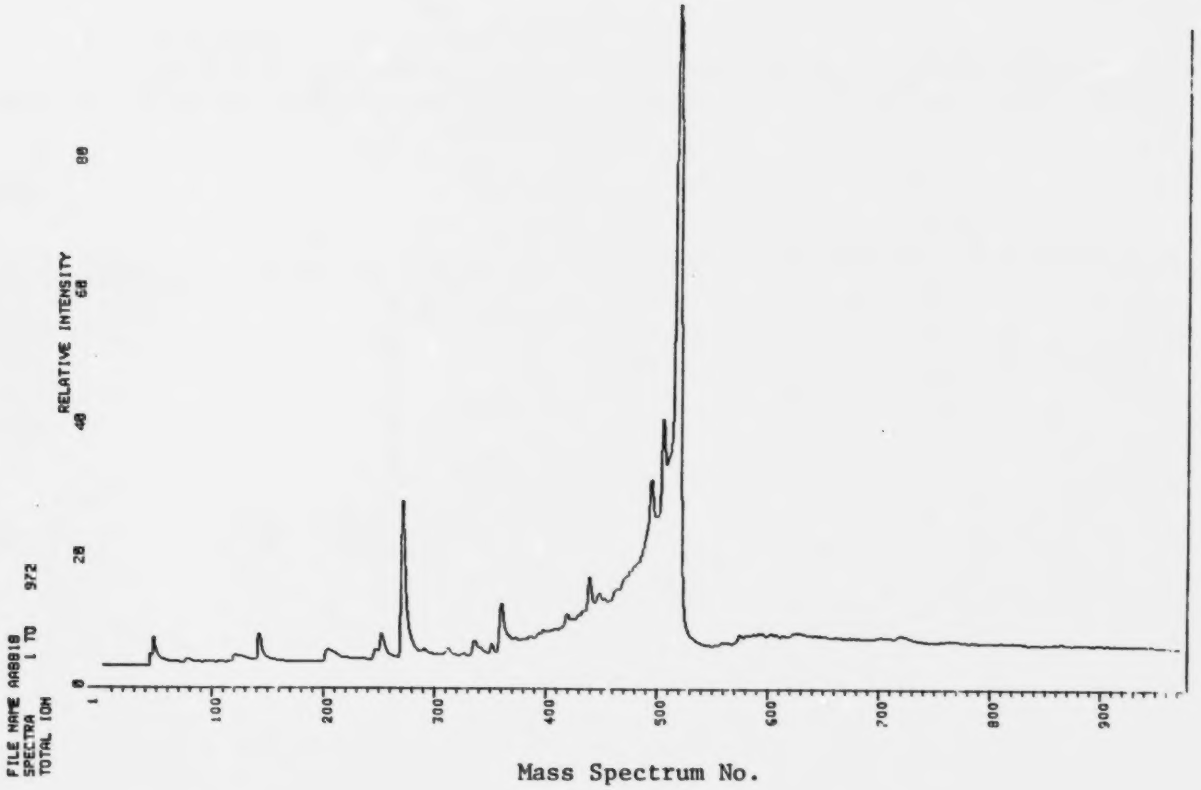

Figure A50. Negative chemical ionization GC/MS/COMP profile of GP4 "neutral" fraction of Influent No. 2 sample (SP2100 capillary).

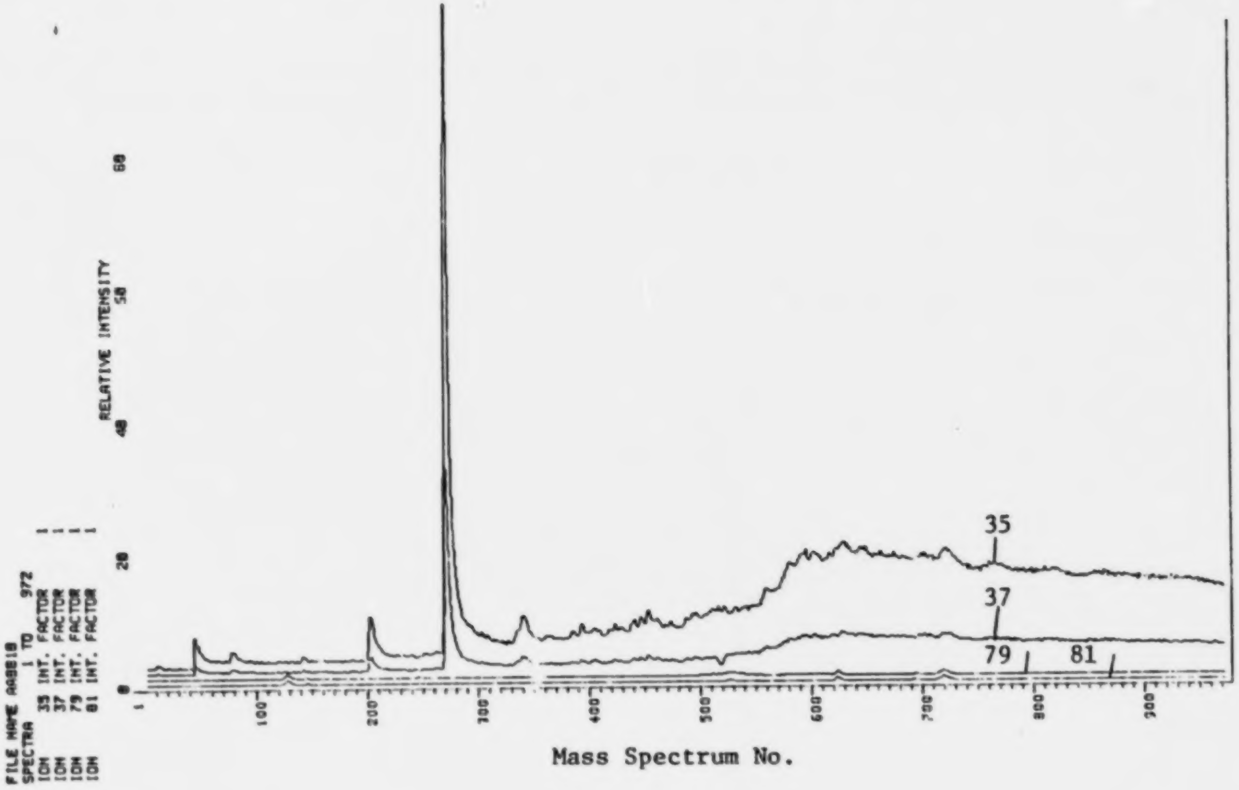

Figure A51. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GP4 "neutral" fraction for Influent No. 2 sample (SP2100 capillary).

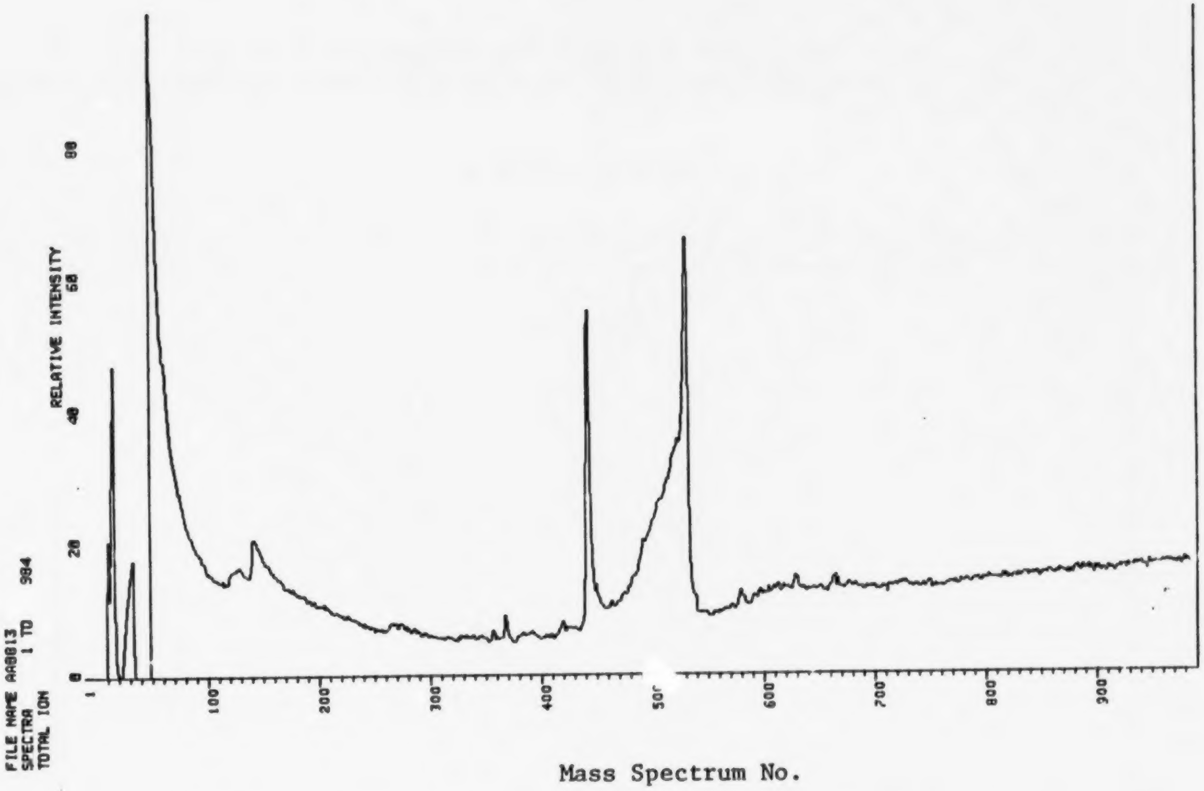

Figure A52. Electron impact GC/MS/COMP profile of GP4 "neutral" fraction for Influent No. 3 sample (SP2100 capillary).

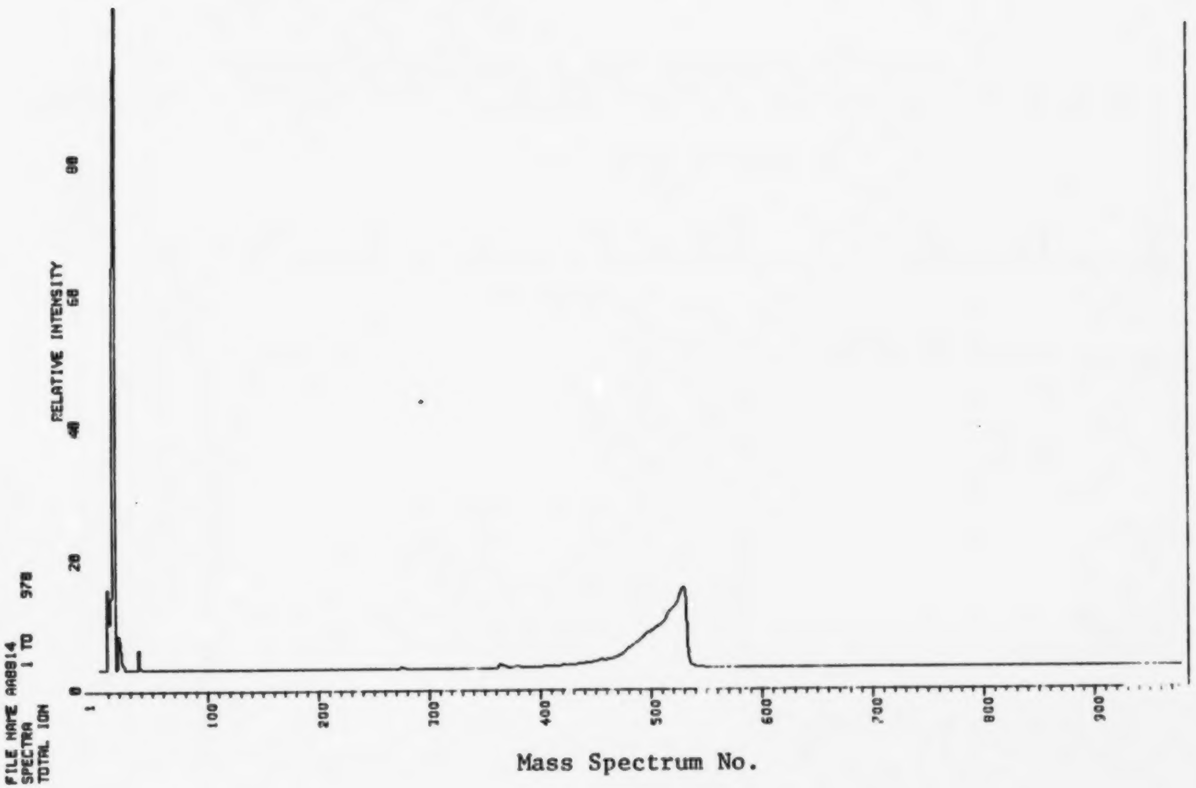

Figure A53. Negative chemical ionization GC/MS/COMP profile of GP4 "neutral" fraction for Influent No. 3 (SP2100 capillary).

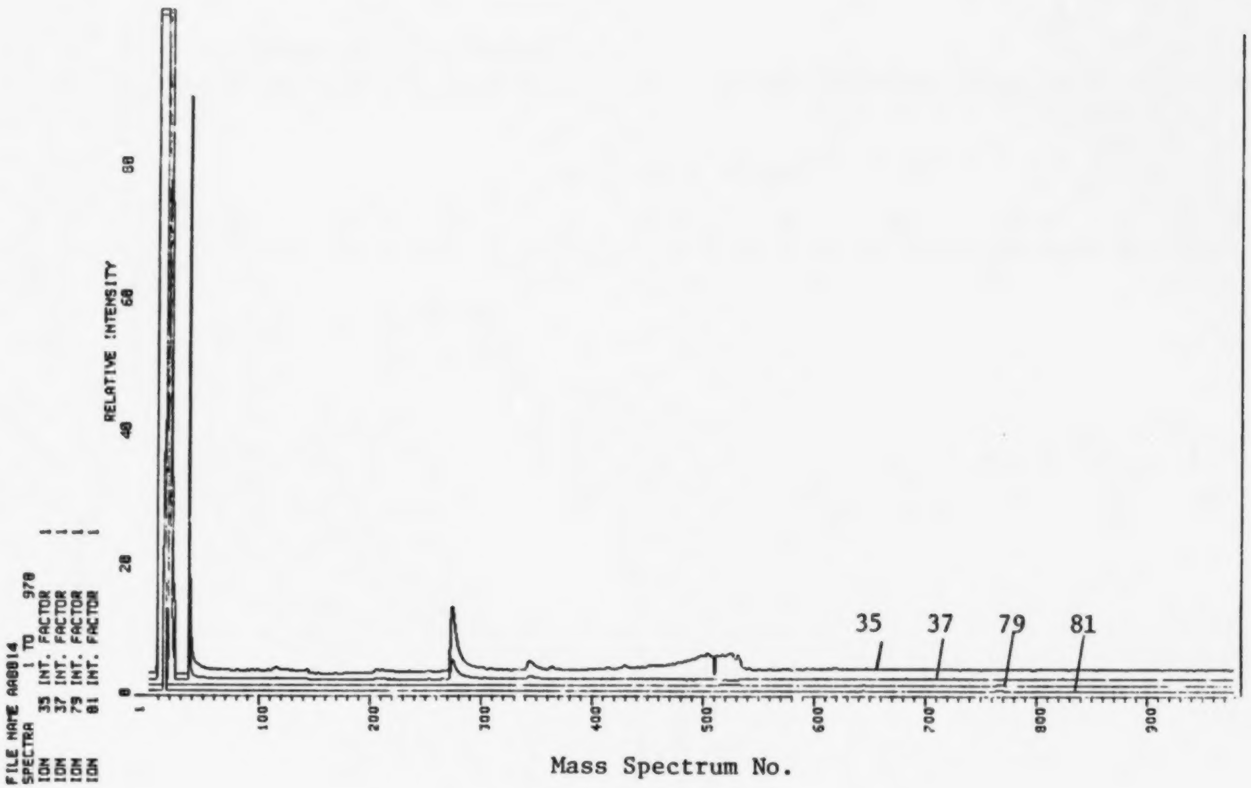

Figure A54. Negative chemical ionization GC/MS/COMP single ion profiles of "neutral" fraction for Influent No. [illegible] sample (SP2100 capillary).

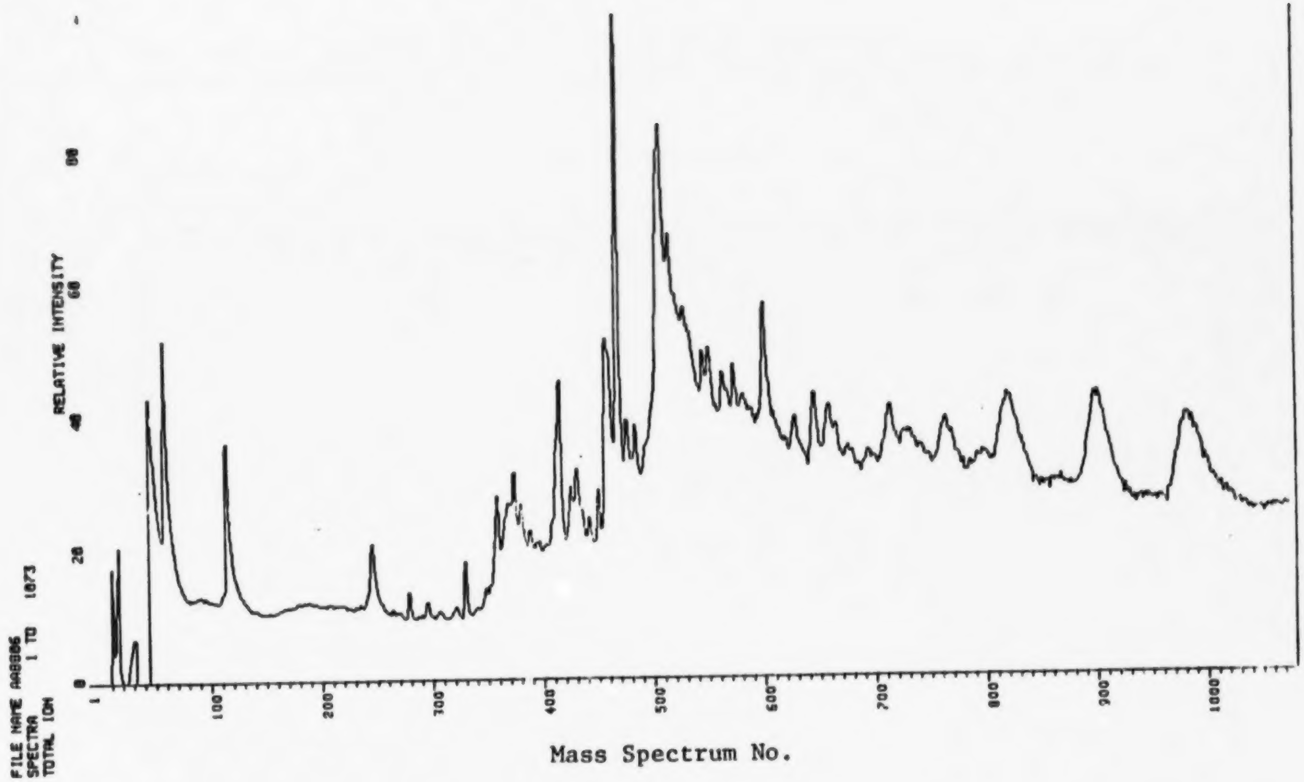

Figure A55. Electron impact GC/MS/COMP profile of GP1 "neutral" fraction for Effluent No. 2 sample (SP2100 capillary).

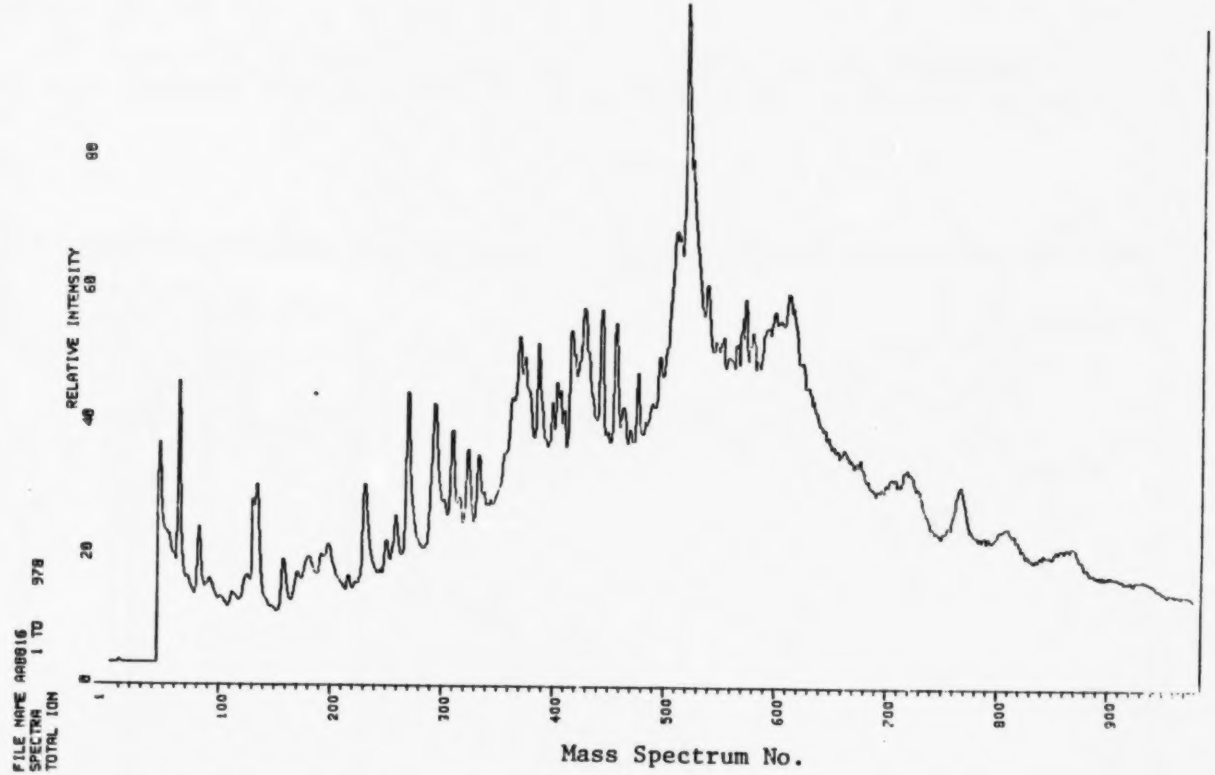

Figure A56. Negative chemical ionization GC/MS/COMP profile of GP1 "neutral" fraction for Effluent No. 2 sample (SP2100 capillary).

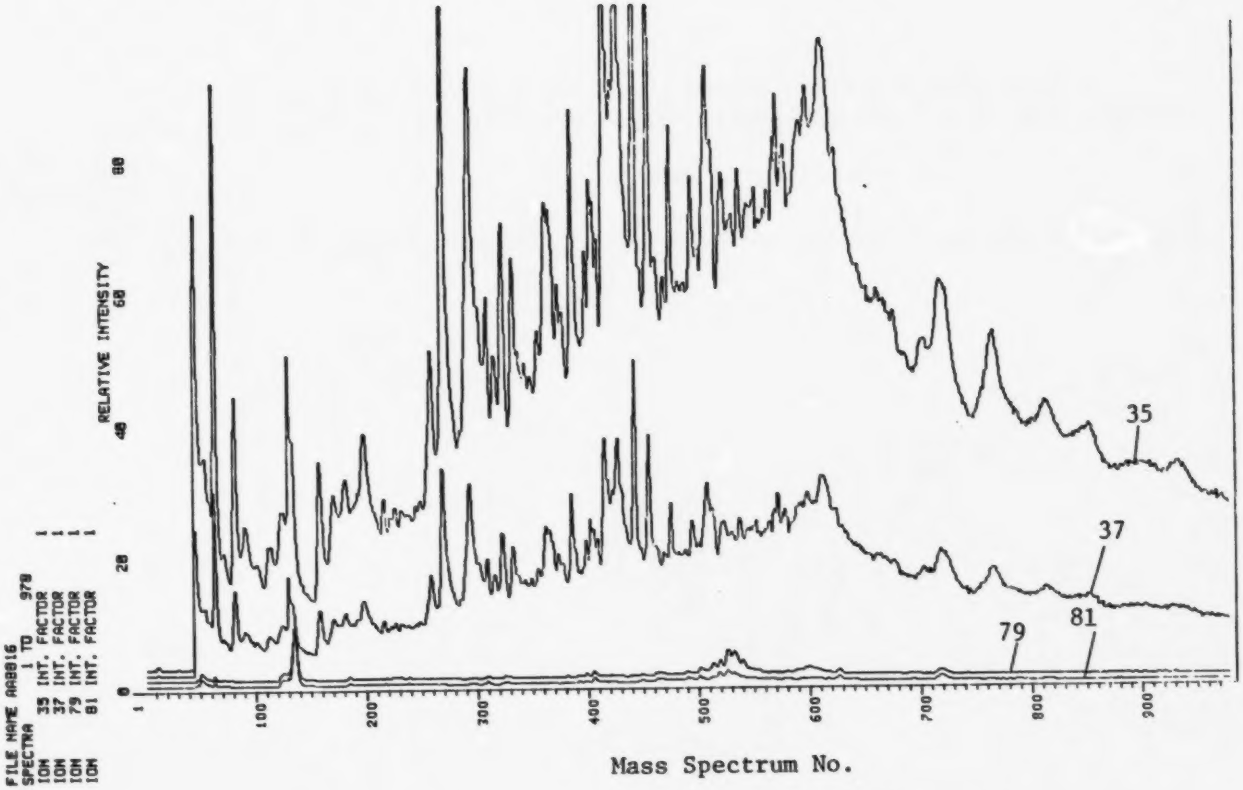

Figure A57. Negative chemical ionization GC/MS/COMP single ion profiles of GP1 "neutral" fraction for Effluent No. 2 sample (SP2100 capillary).

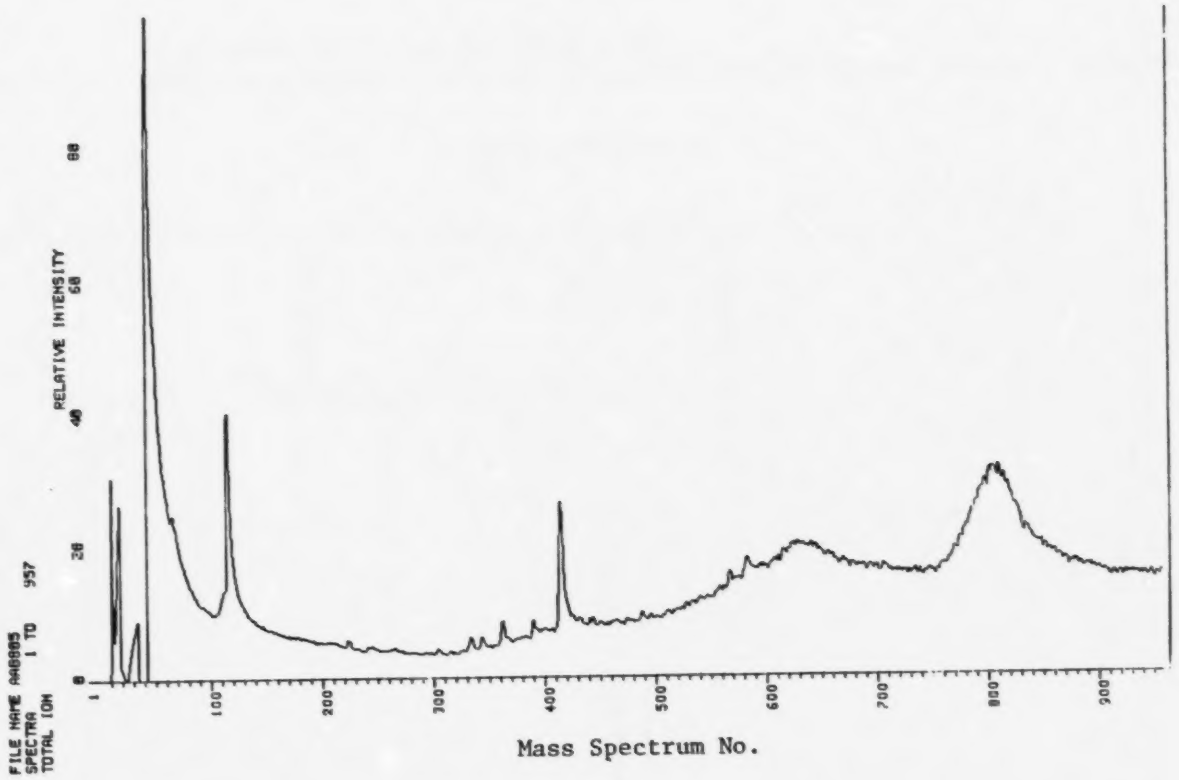

Figure A58. Electron impact GC/MS/COMP profile of GP4 "neutral" fraction for Effluent No. 2 (SP2100 capillary).

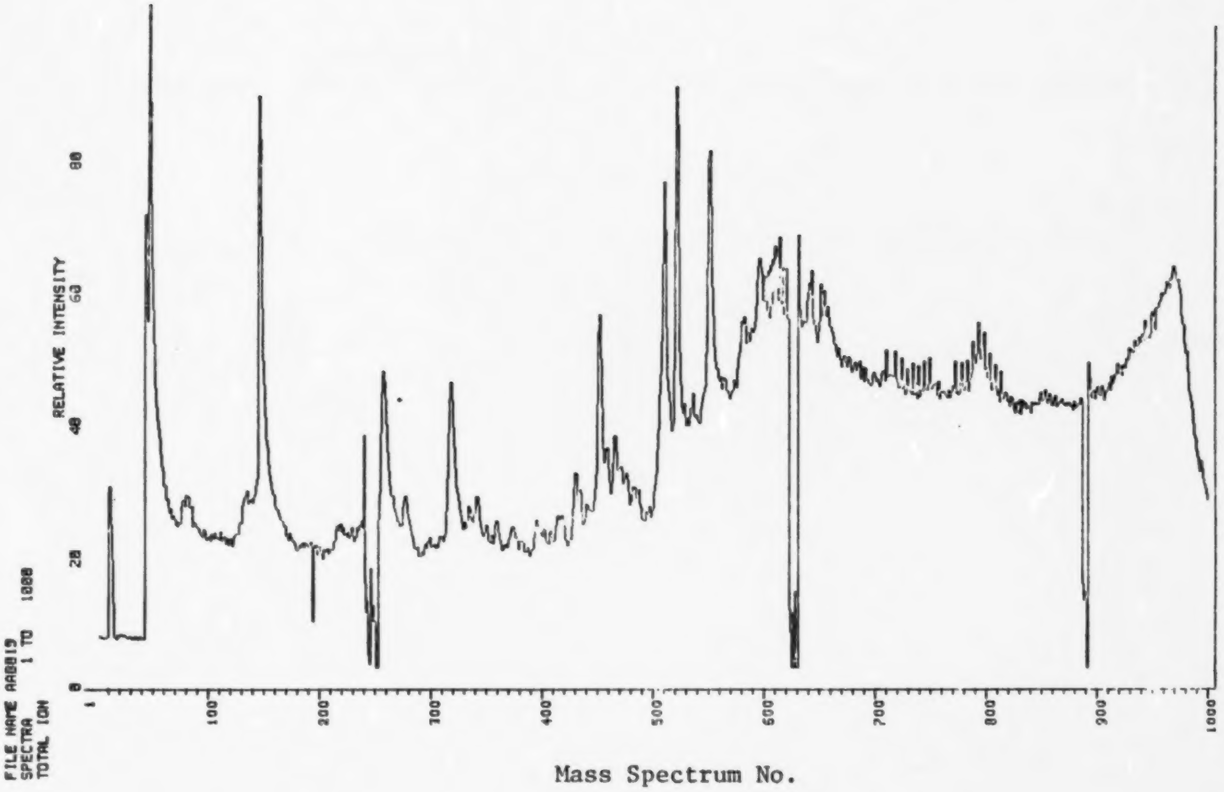

Figure A59. Negative chemical ionization GC/MS/COMP profile of GP4 "neutral" fraction of Effluent No. 2 (SP2100 capillary).

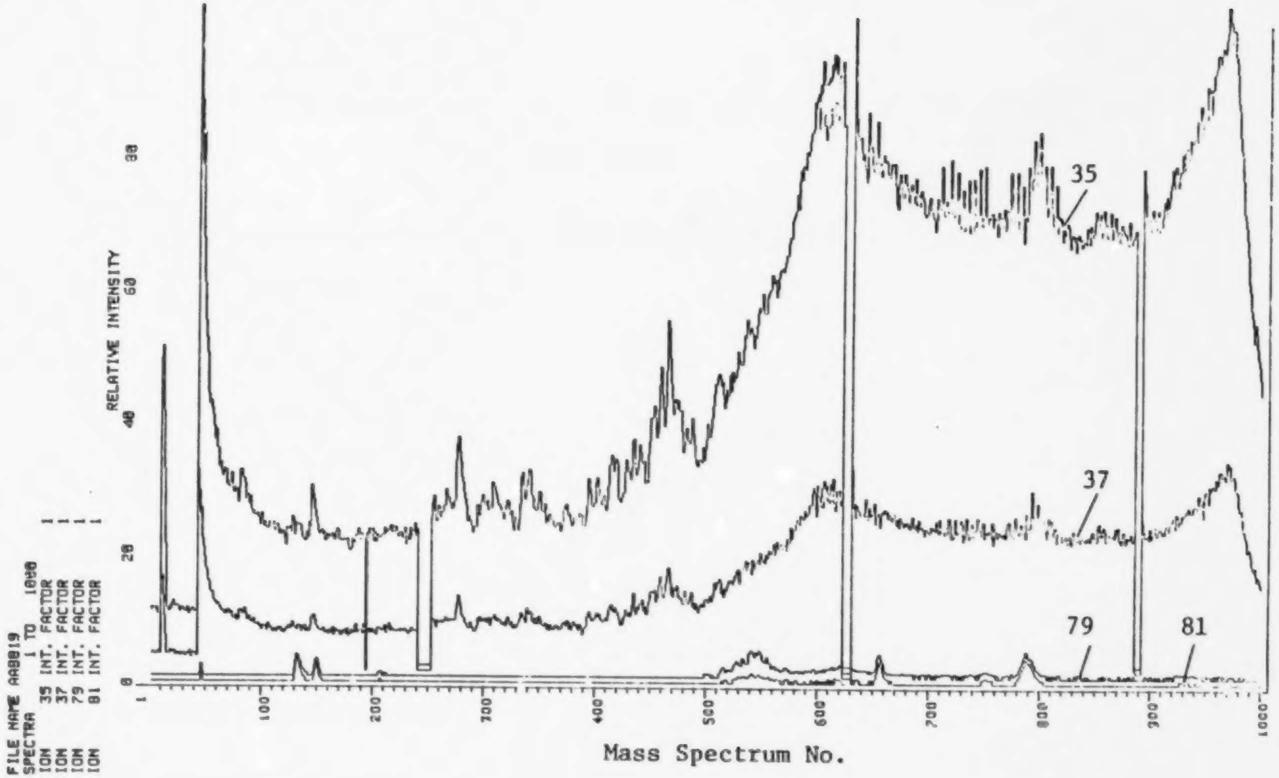

Figure A60. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GP4 "neutral" fraction of Effluent No. 2 (SP2100 capillary).

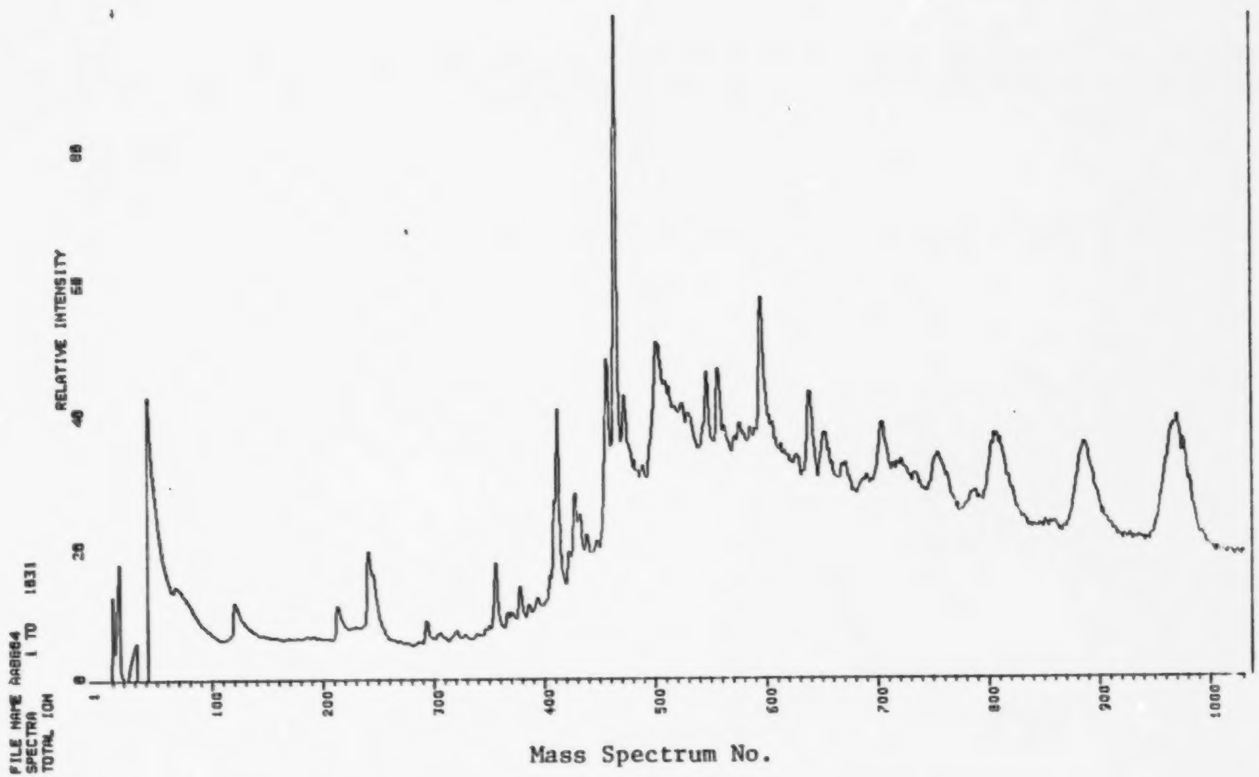

Figure A61. Electron impact GC/MS/COMP profile of GP1 "neutral" fraction for Effluent No. 3 (SP2100 capillary).

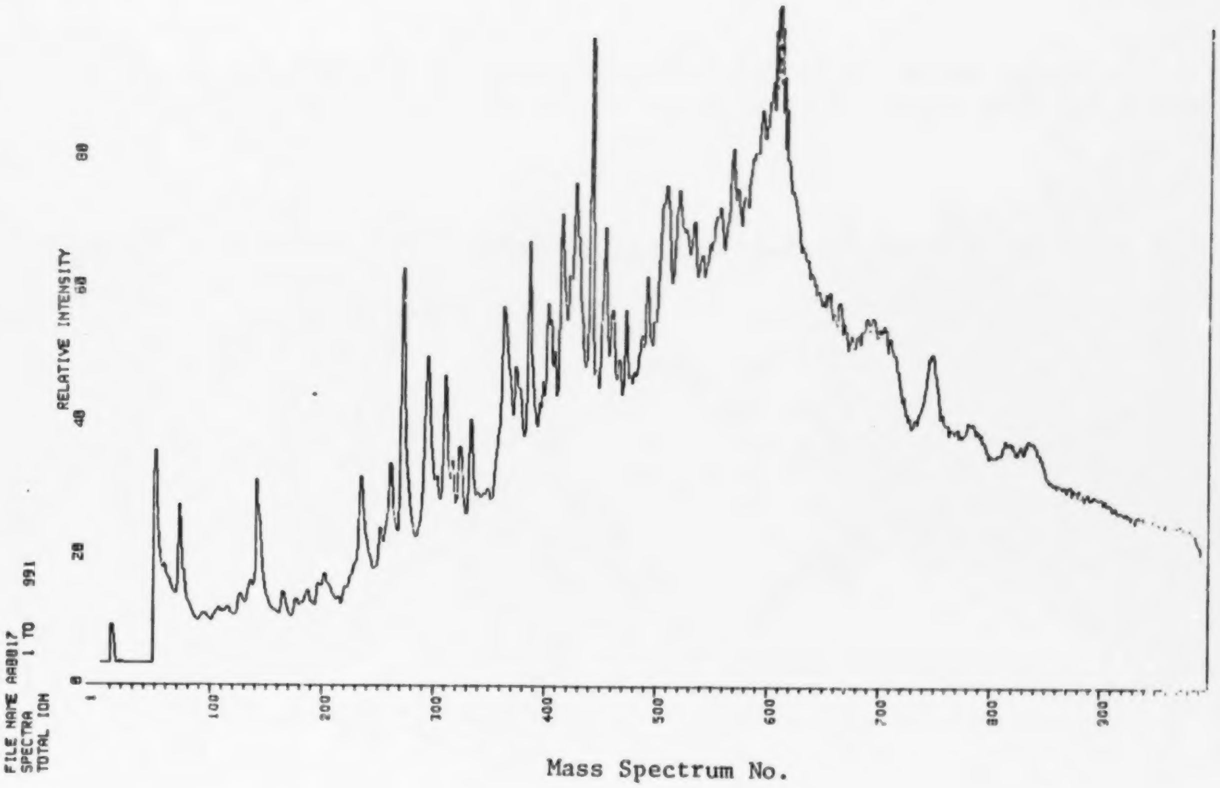

Figure A62. Negative chemical ionization GC/MS/COMP profile of GP1 "neutral" fraction of Effluent No. 3 (SP2100 capillary).

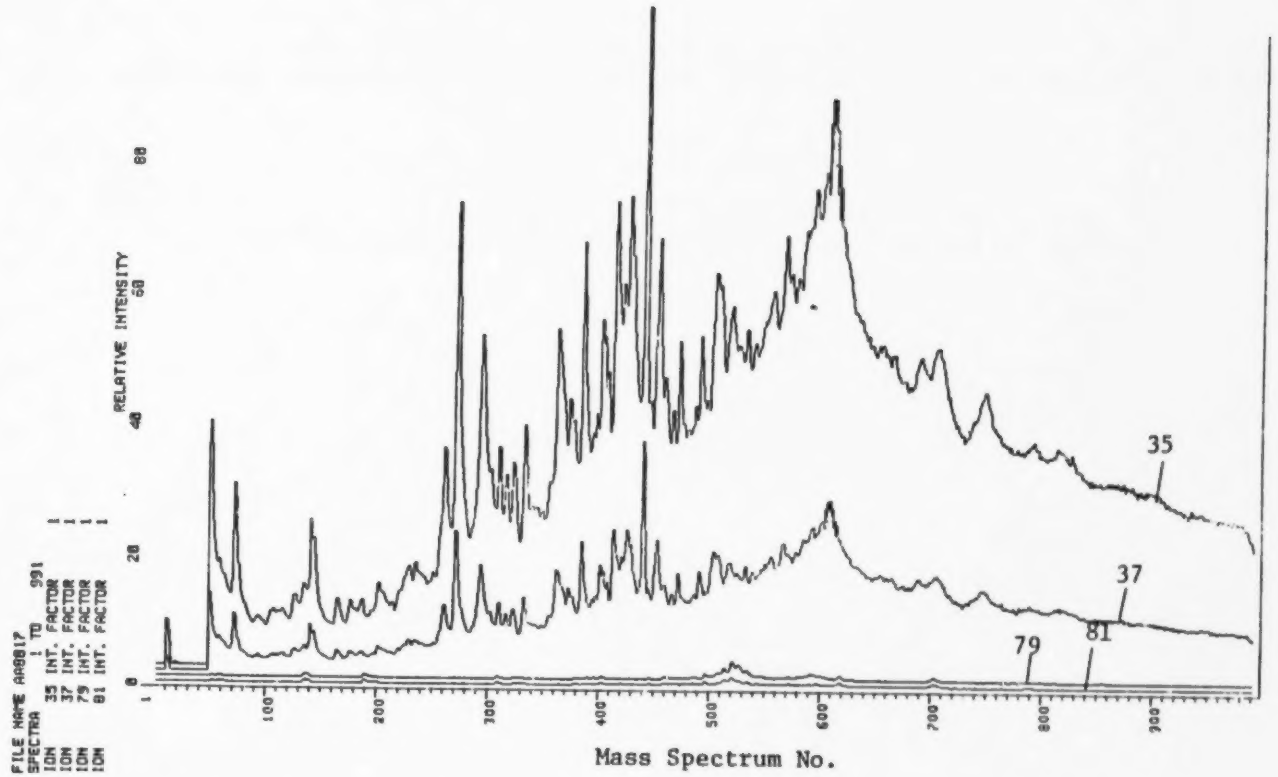

Figure A63. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GP1 "neutral" fraction for Effluent No. 3 (SP2100 capillary).

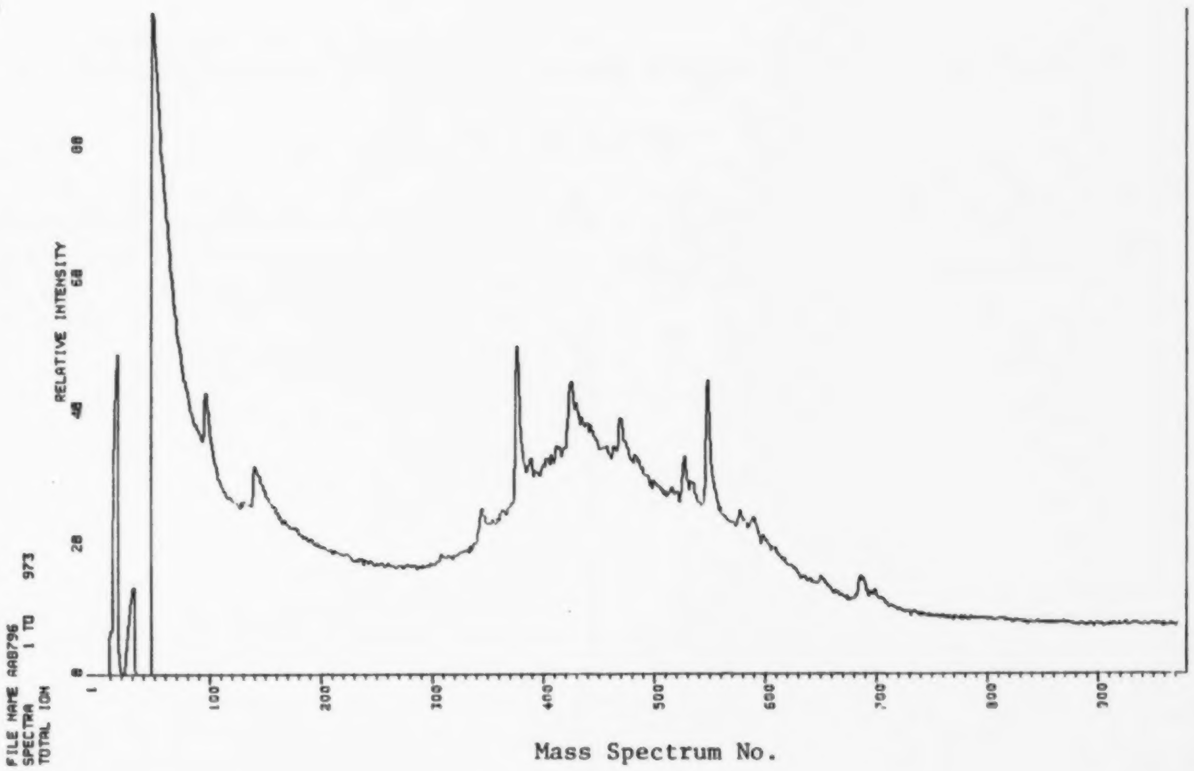

Figure A64. Electron impact GC/MS/COMP profile of GP4 "neutral" fraction for Effluent No. 3 sample (SP2100 capillary).

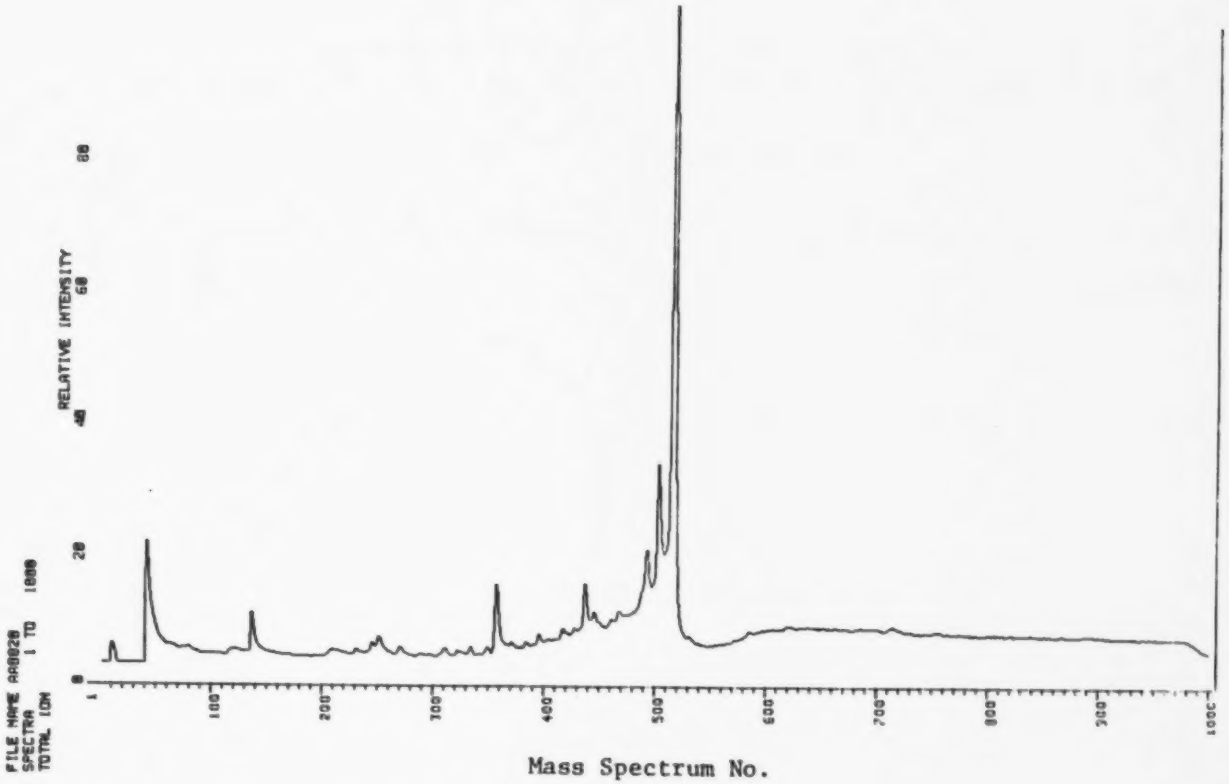

Figure A65. Negative chemical ionization GC/MS/COMP profile of GP4 "neutral" fraction for Effluent No. 3 (SP2100 capillary).

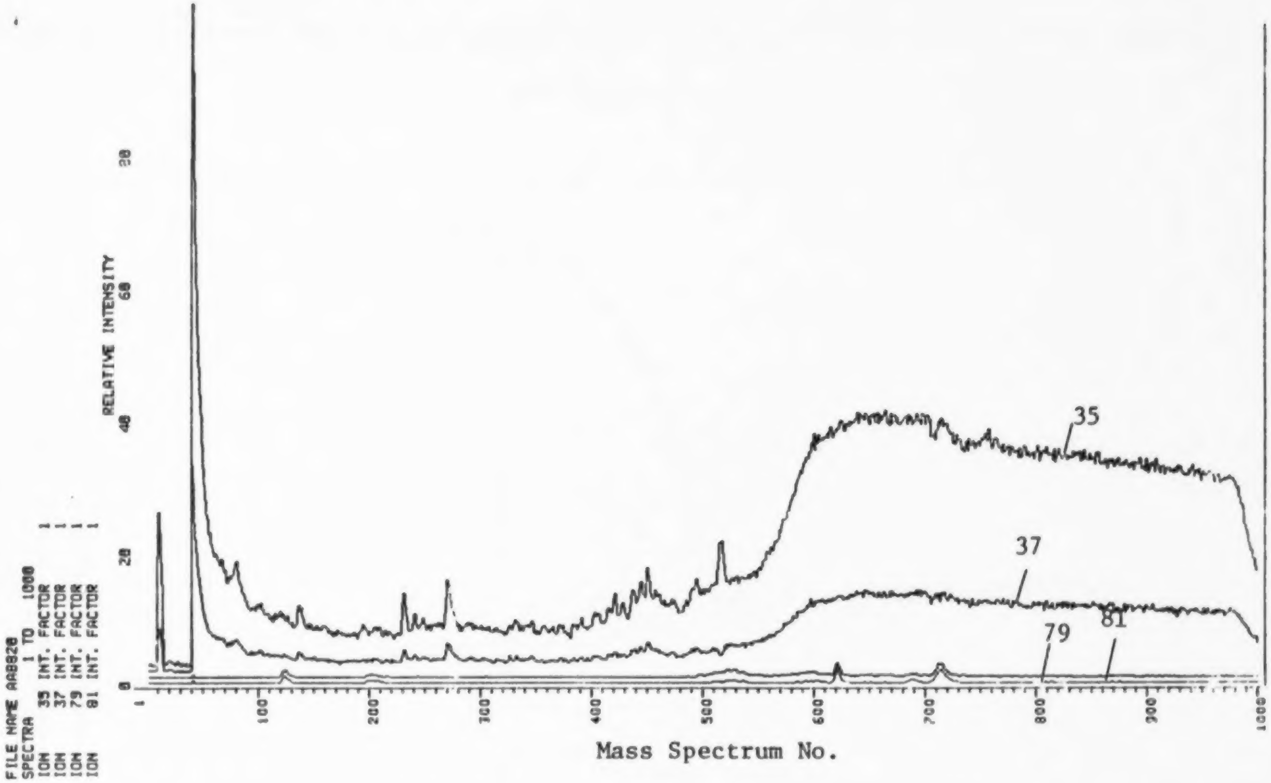

Figure A66. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GP4 "neutral" fraction for Effluent No. 3 (SP2100 capillary).

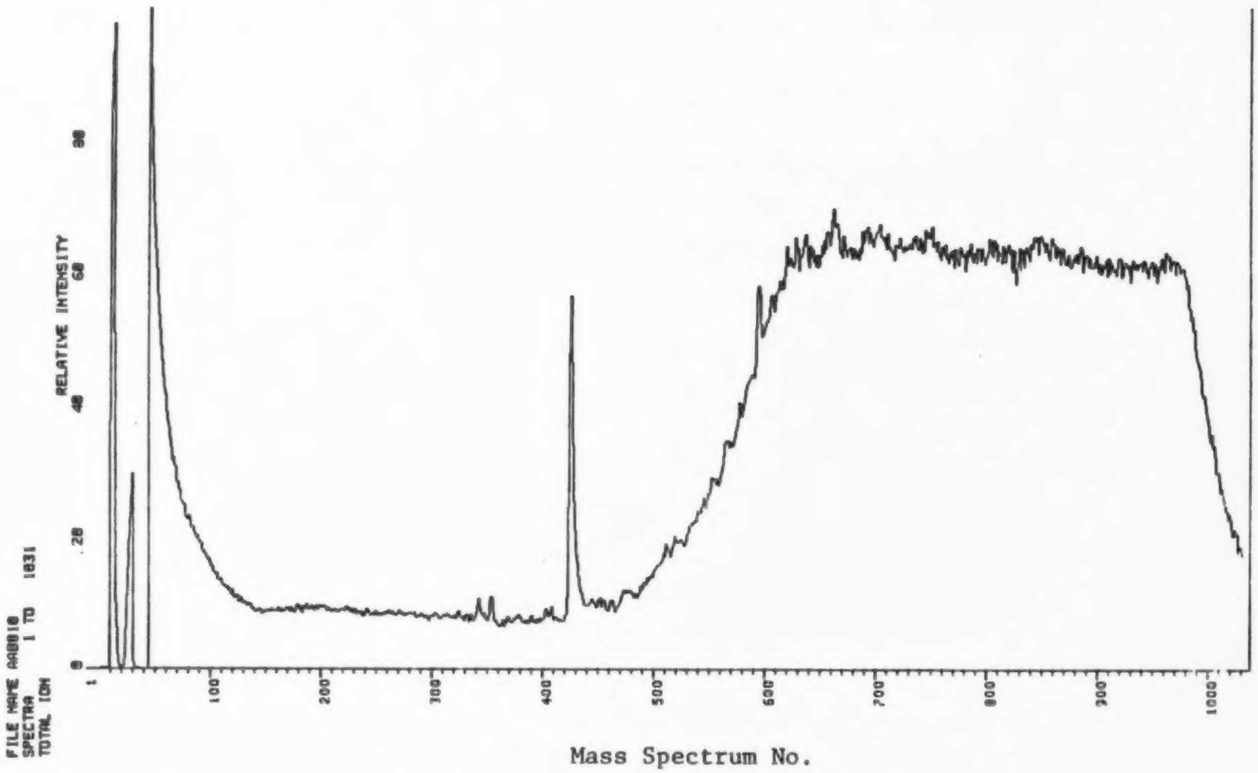

Figure A67. Electron impact GC/MS/COMP profile of GP1 "neutral" solvent blank (SP2100 capillary).

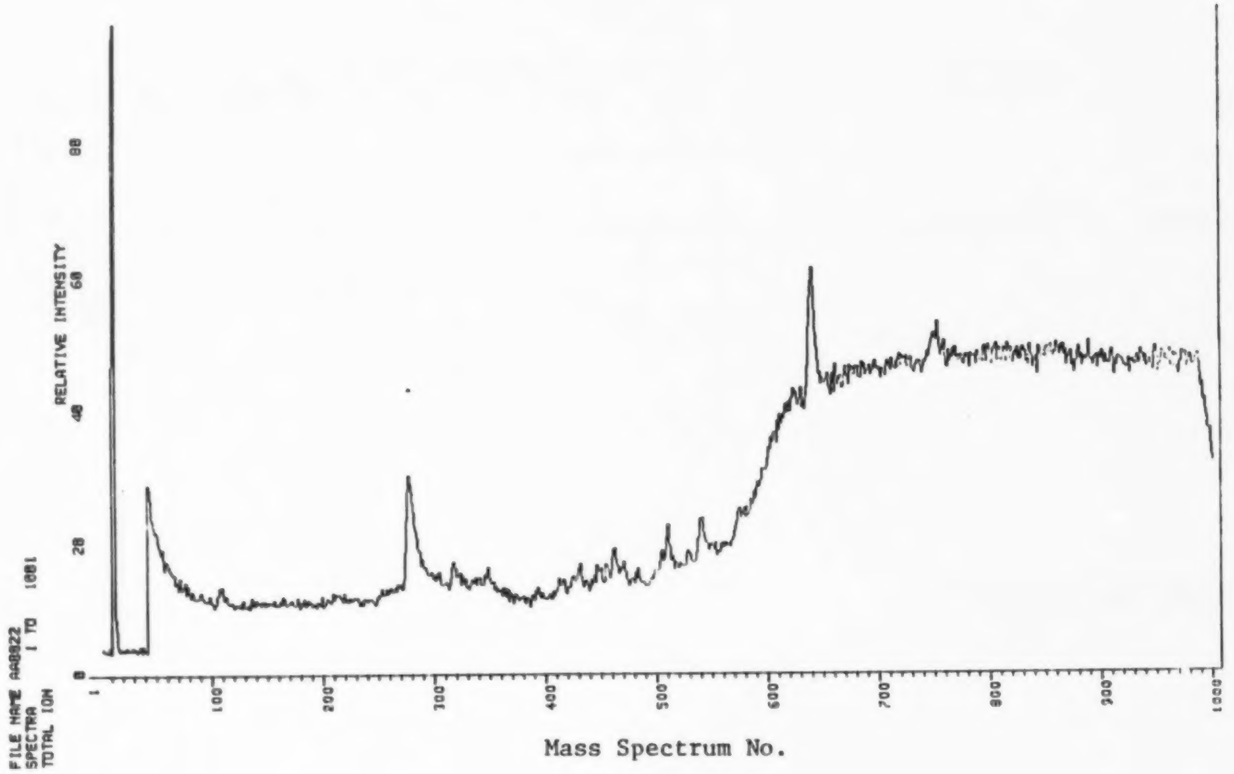

Figure A68. Negative chemical ionization GC/MS/COMP profile of GP1 "neutral" solvent blank (SP2100 capillary).

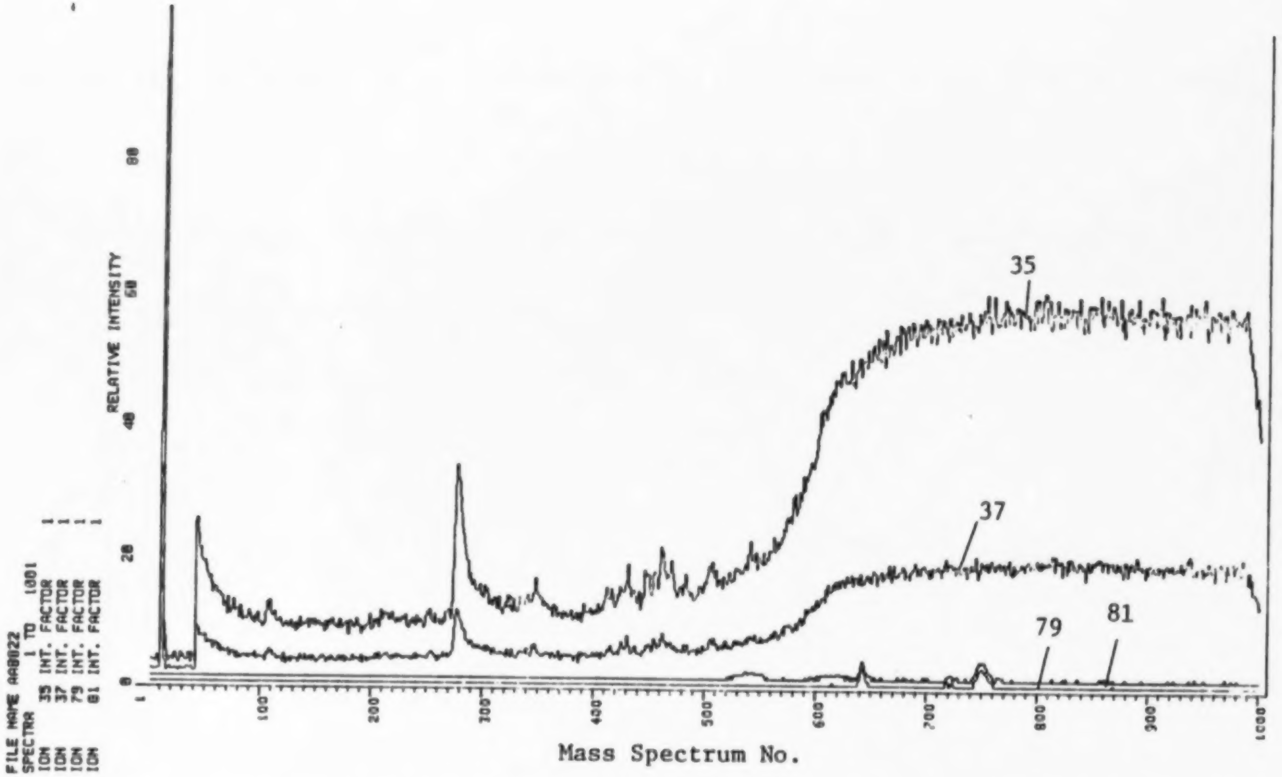

Figure A69. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GP1 "neutral" solvent blank (SP2100 capillary).

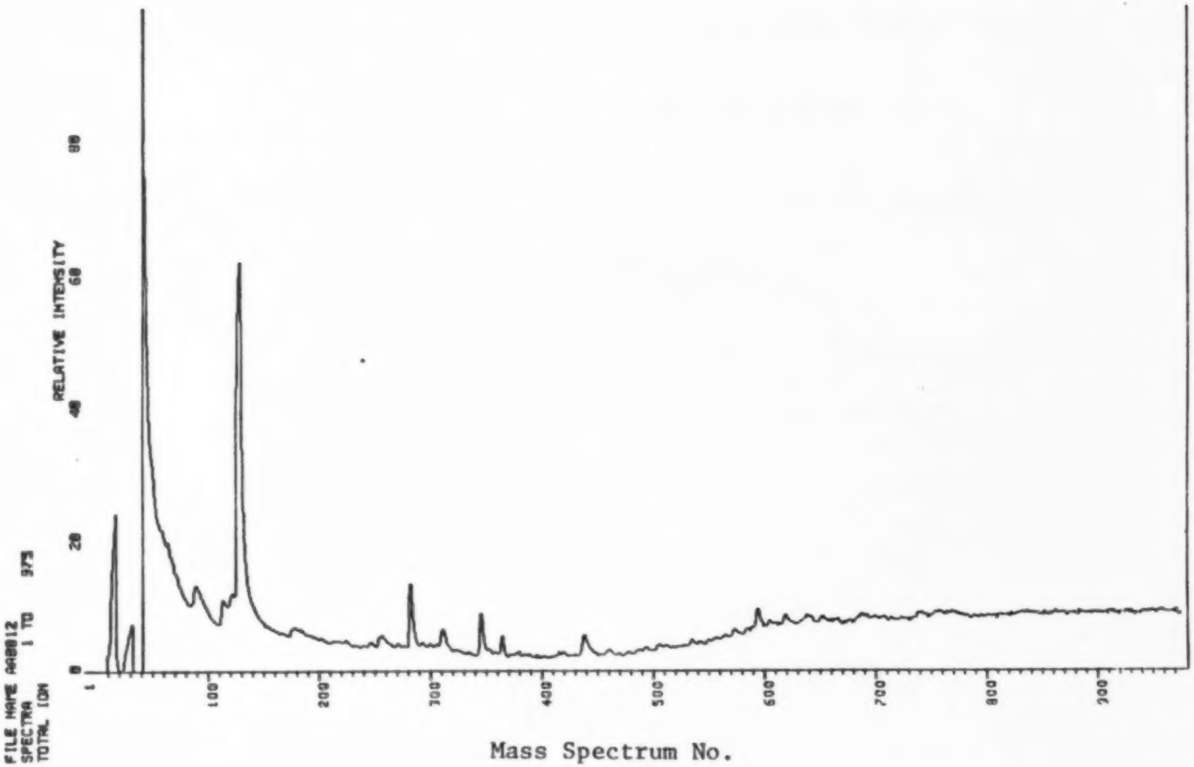

Figure A70. Electron impact GC/MS/COMP profile of GP4 "neutral" solvent blank (SP2100 capillary).

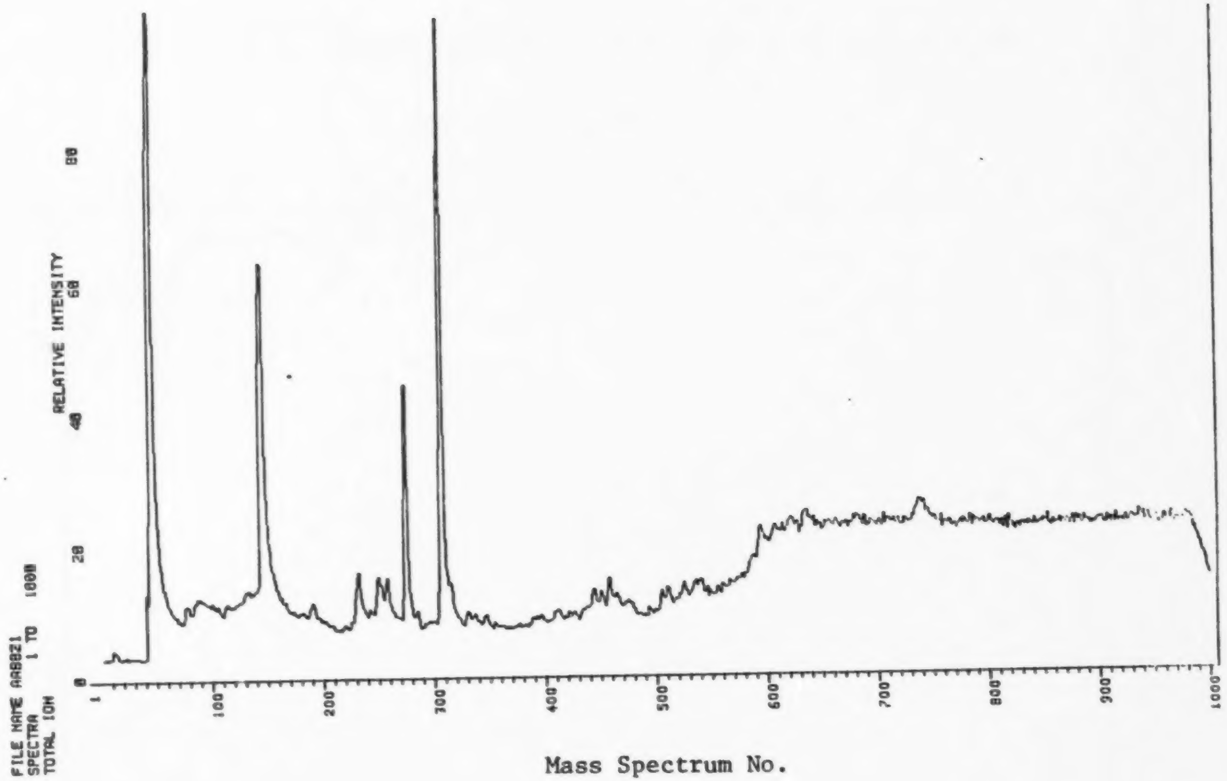

Figure A71. Negative chemical ionization GC/MS/COMP profile of GP4 "neutral" solvent blank (SP2100 capillary).

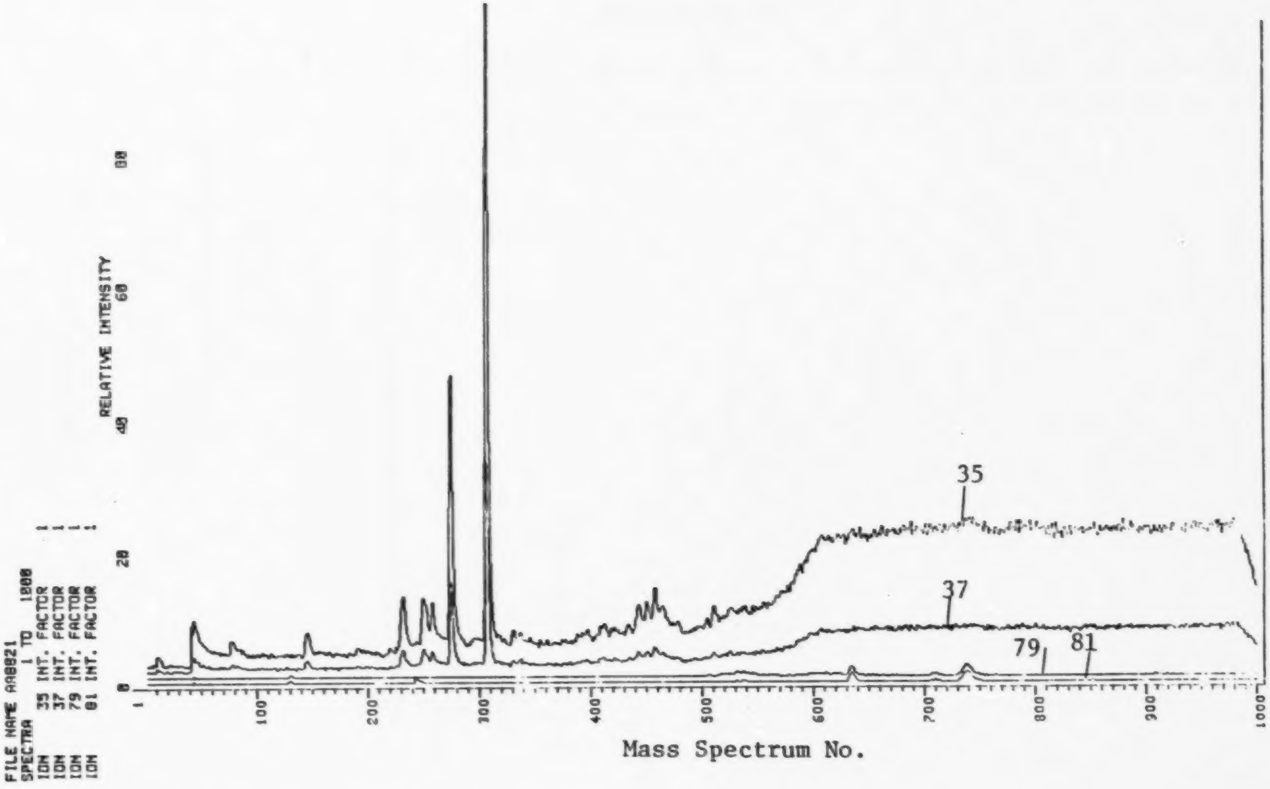

Figure A72. Negative chemical ionization GC/MS/COMP single ion profiles of GP4 "neutral" solvent blank (SP2100 capillary).

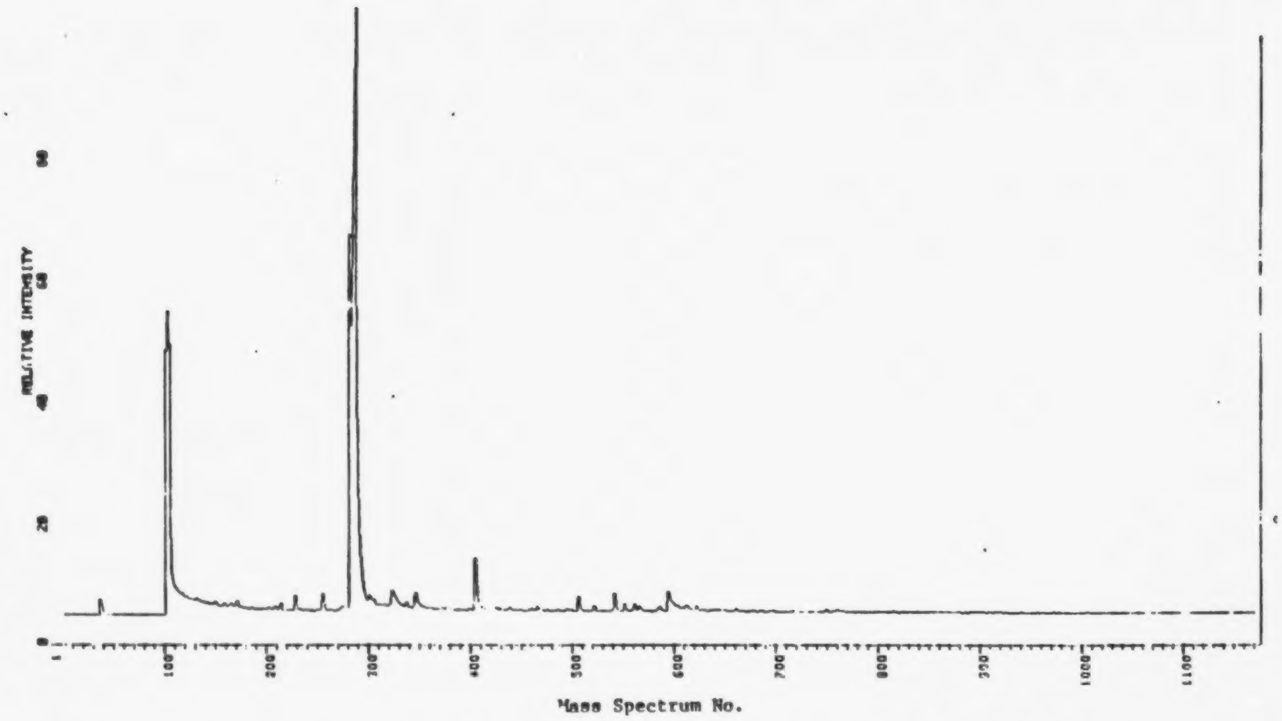

Figure A73. Negative chemical ionization GC/MS/COMP profile of GPA 1 "acid" fraction for Influent No. 1 sample from superchlorination process.

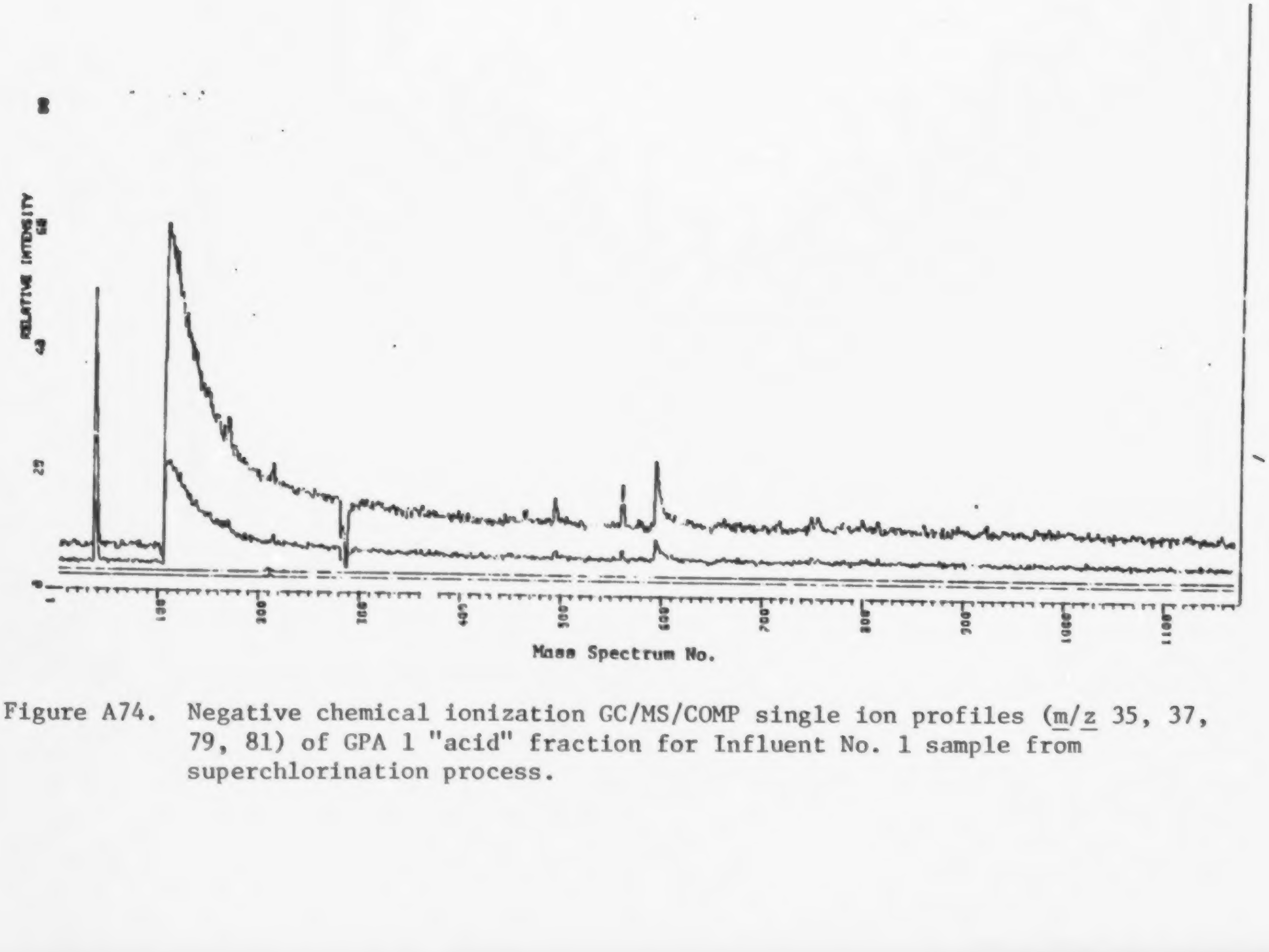

Figure A74. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GPA 1 "acid" fraction for Influent No. 1 sample from superchlorination process.

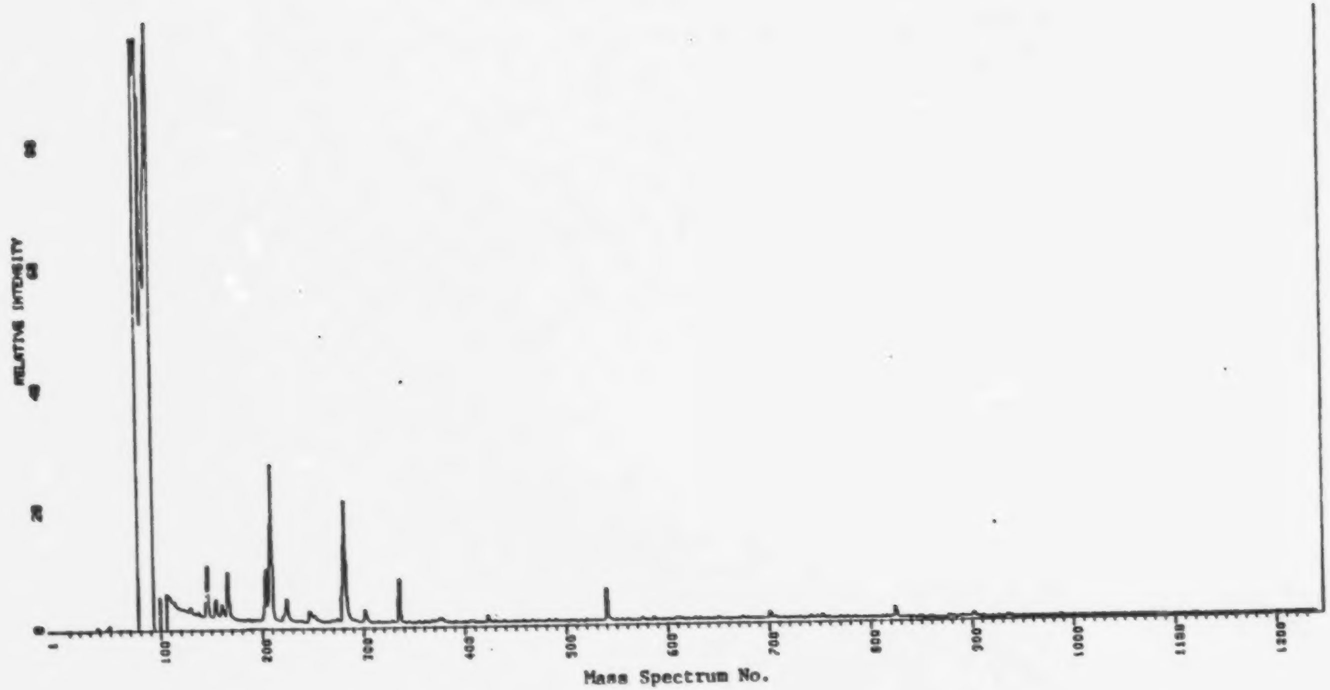

Figure A75. Electron impact GC/MS/COMP profile of GPA 1 fraction for Influent No. 2 from superchlorination process.

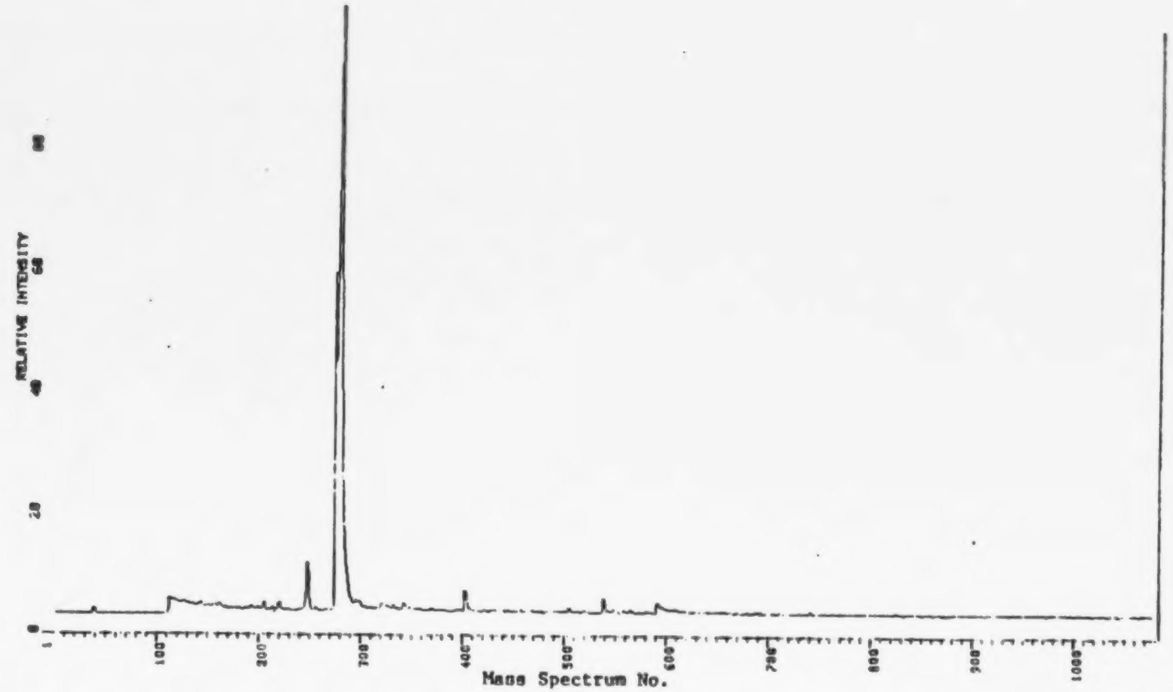

Figure A76. Negative chemical ionization GC/MS/COMP profile of GPA 1 fraction for Influent No. 2 from superchlorination process.

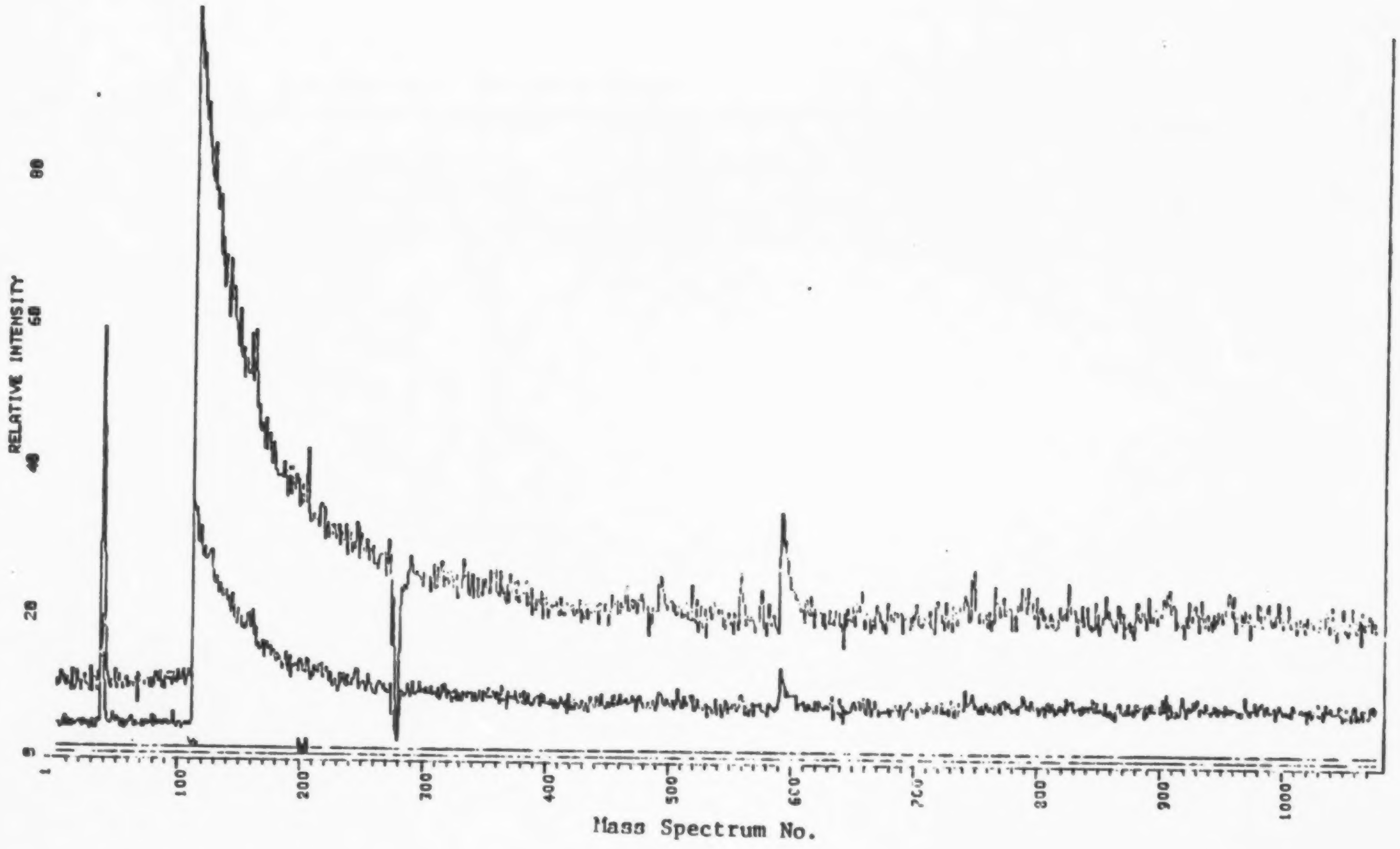

Figure A77. Negative chemical ionization GC/MS/COMP single ion profiles ($\underline{m}/\underline{z}$ 35, 37, 79, 81) of GPA 1 fraction for Influent No. 2 from superchlorination process.

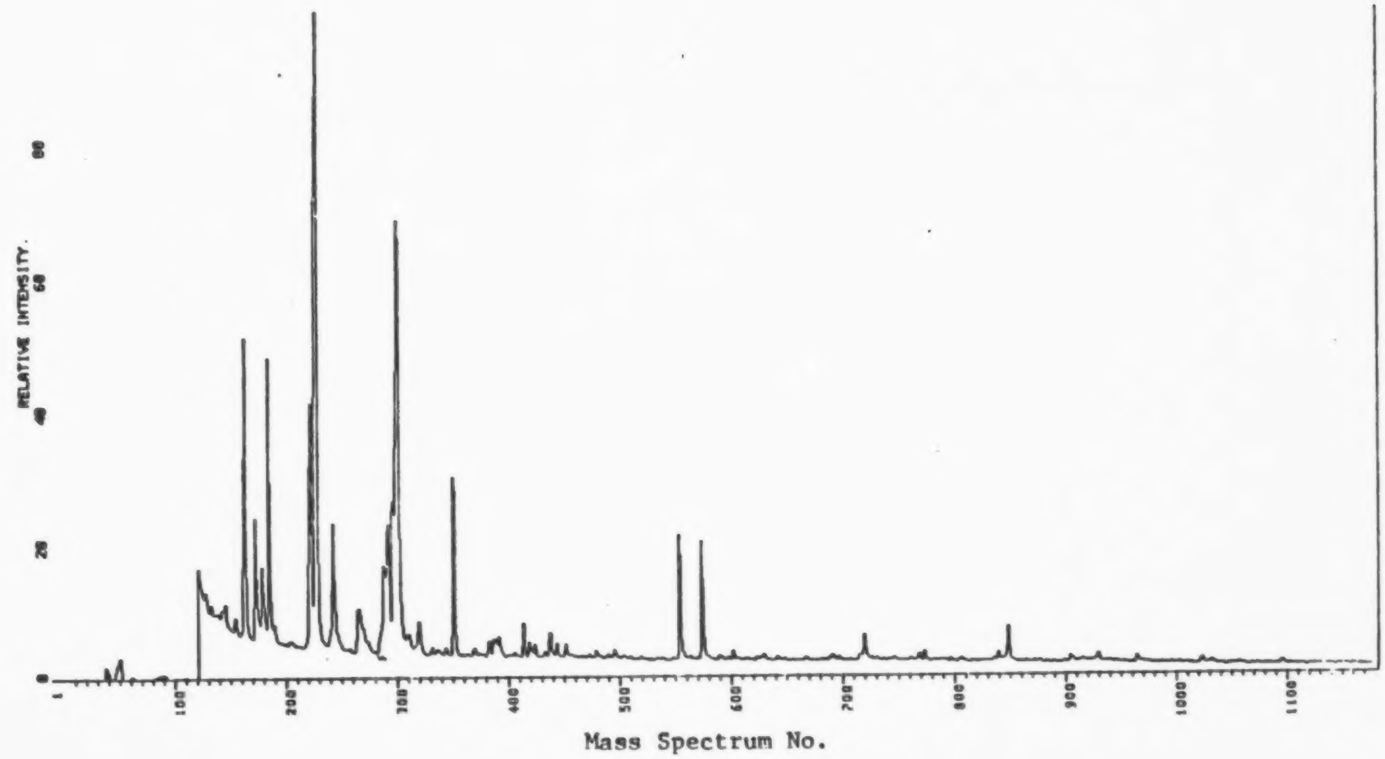

Figure A78. Electron impact GC/MS/COMP profile of GPA 1 fraction for Influent No. 3 from superchlorination process.

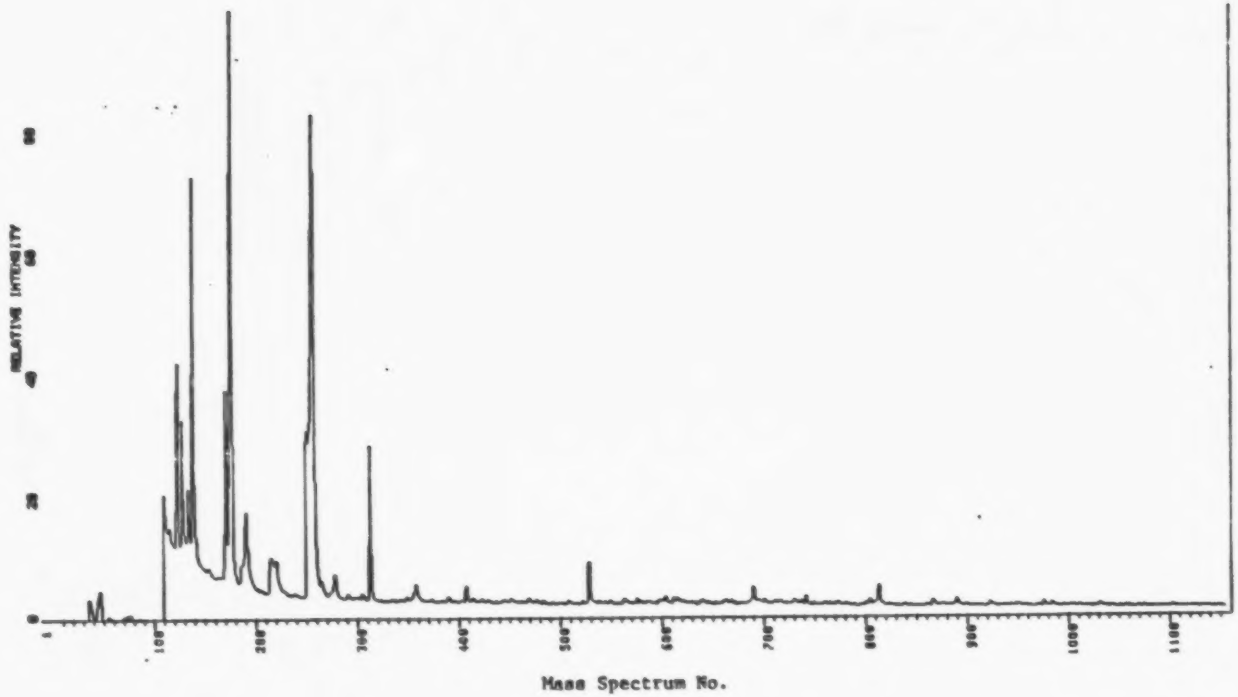

Figure A79. Electron impact GC/MS/COMP profile of GPA 1 for Effluent No. 2 from superchlorination process.

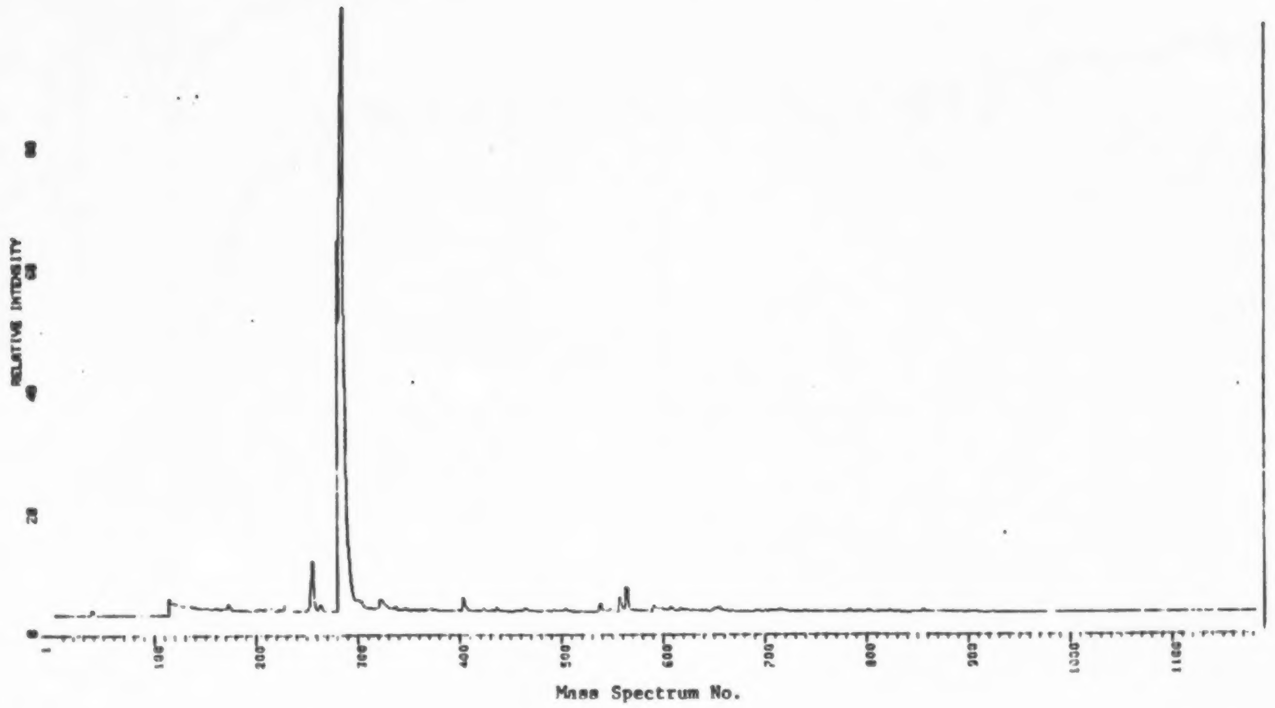

Figure A80. Negative chemical ionization GC/MS/COMP profile of GPA 1 fraction for Effluent No. 2 from superchlorination process.

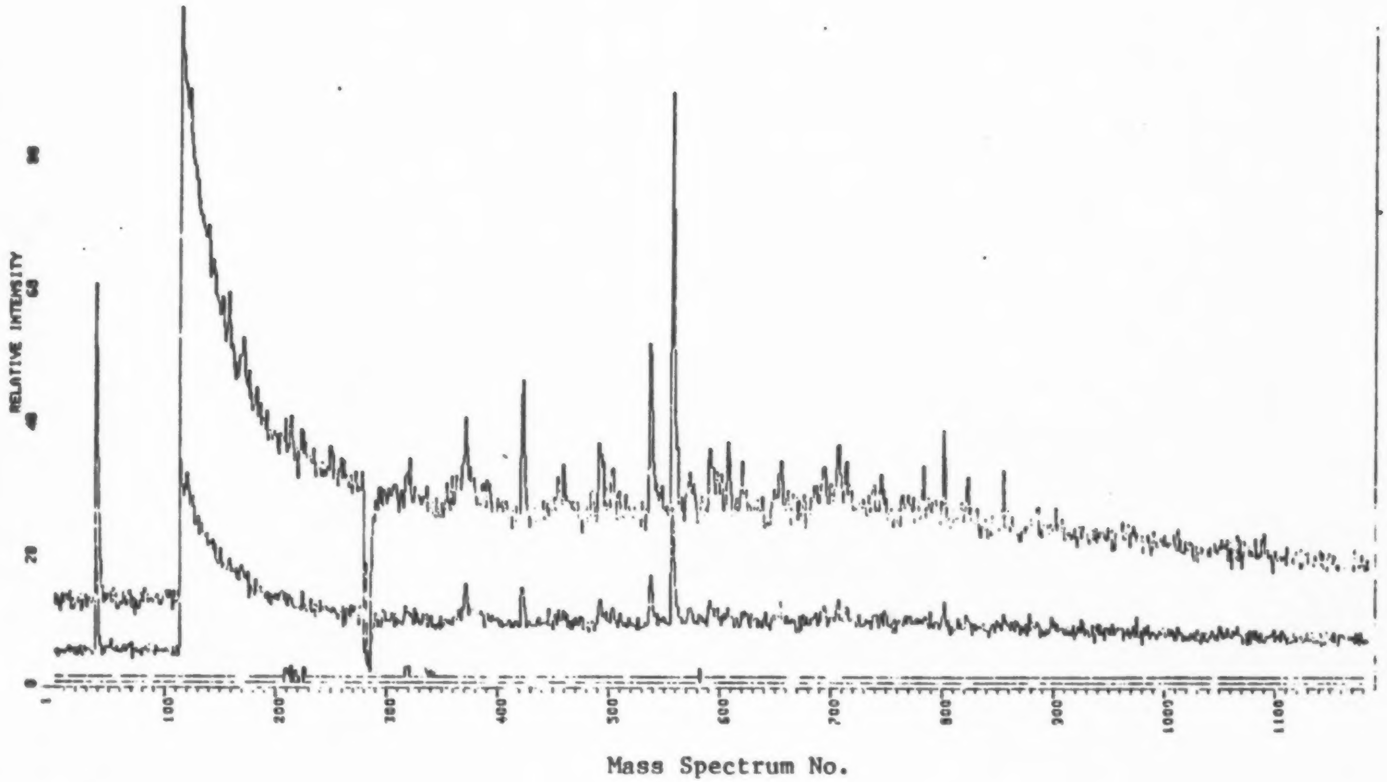

Figure A81. Negative chemical ionization GC/MS/COMP single ion profile (m/z 35, 37, 79, 81) of GPA 1 fraction for Effluent No. 2 from superchlorination process.

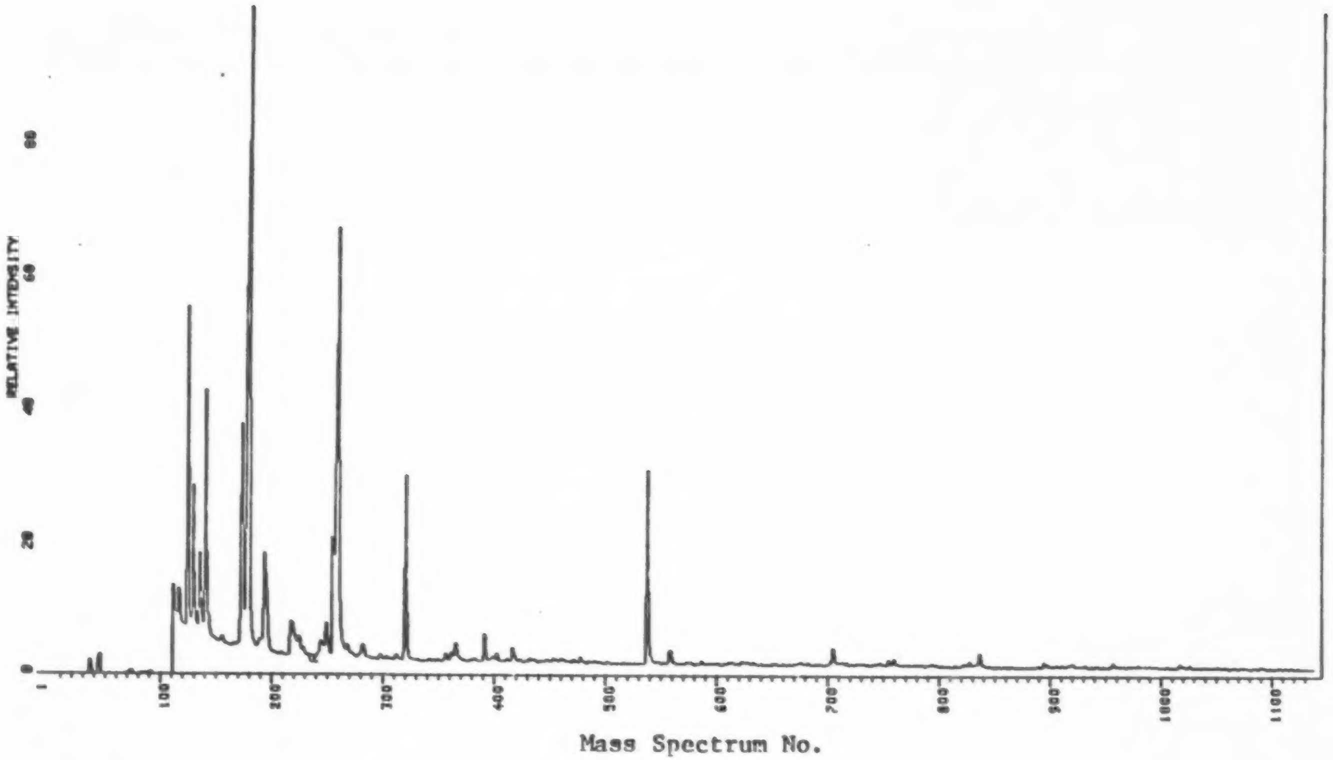

Figure A82. Electron impact GC/MS/COMP profile of GPA 1 fraction from Effluent No. 3 for superchlorination process.

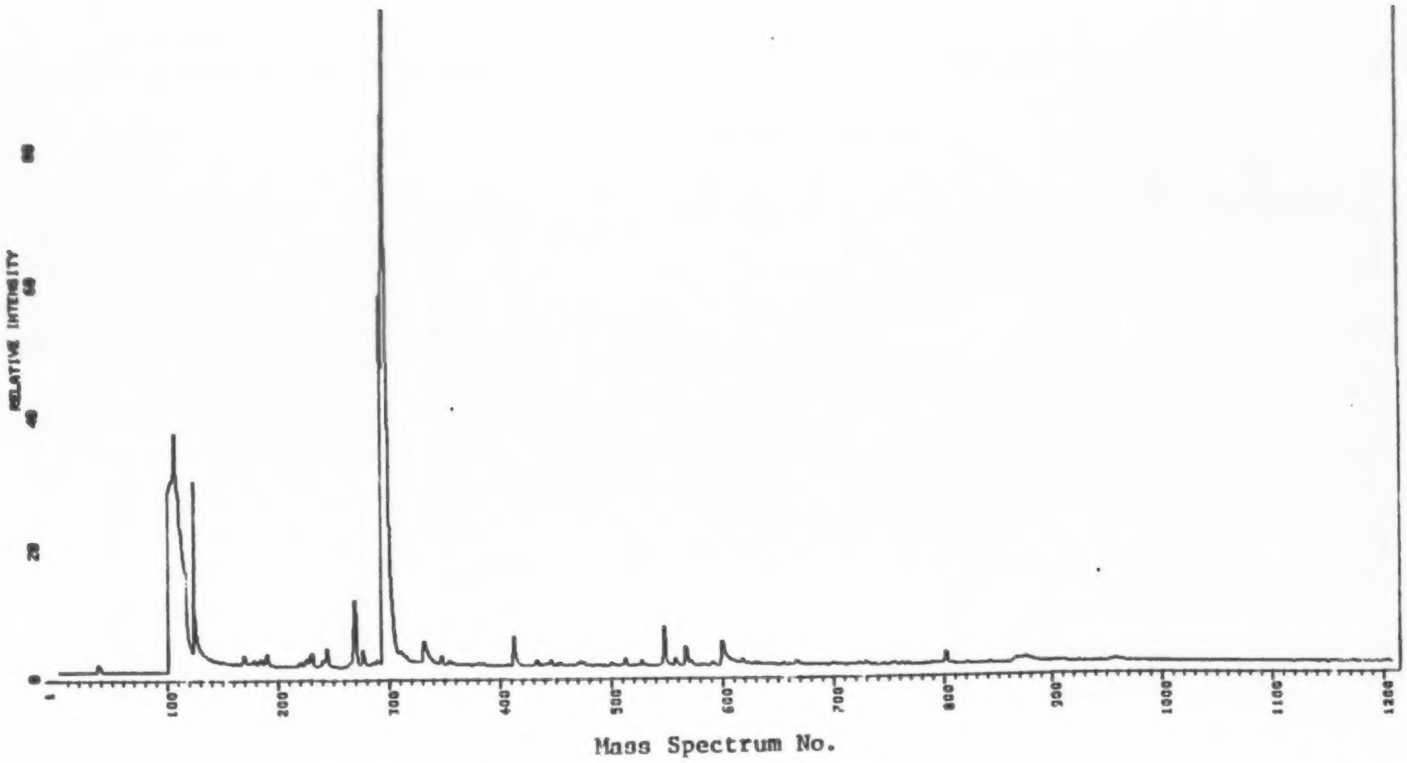

Figure A83. Negative chemical ionization GC/MS/COMP profile of GPA 1 fraction for Effluent No. 3 from superchlorination process.

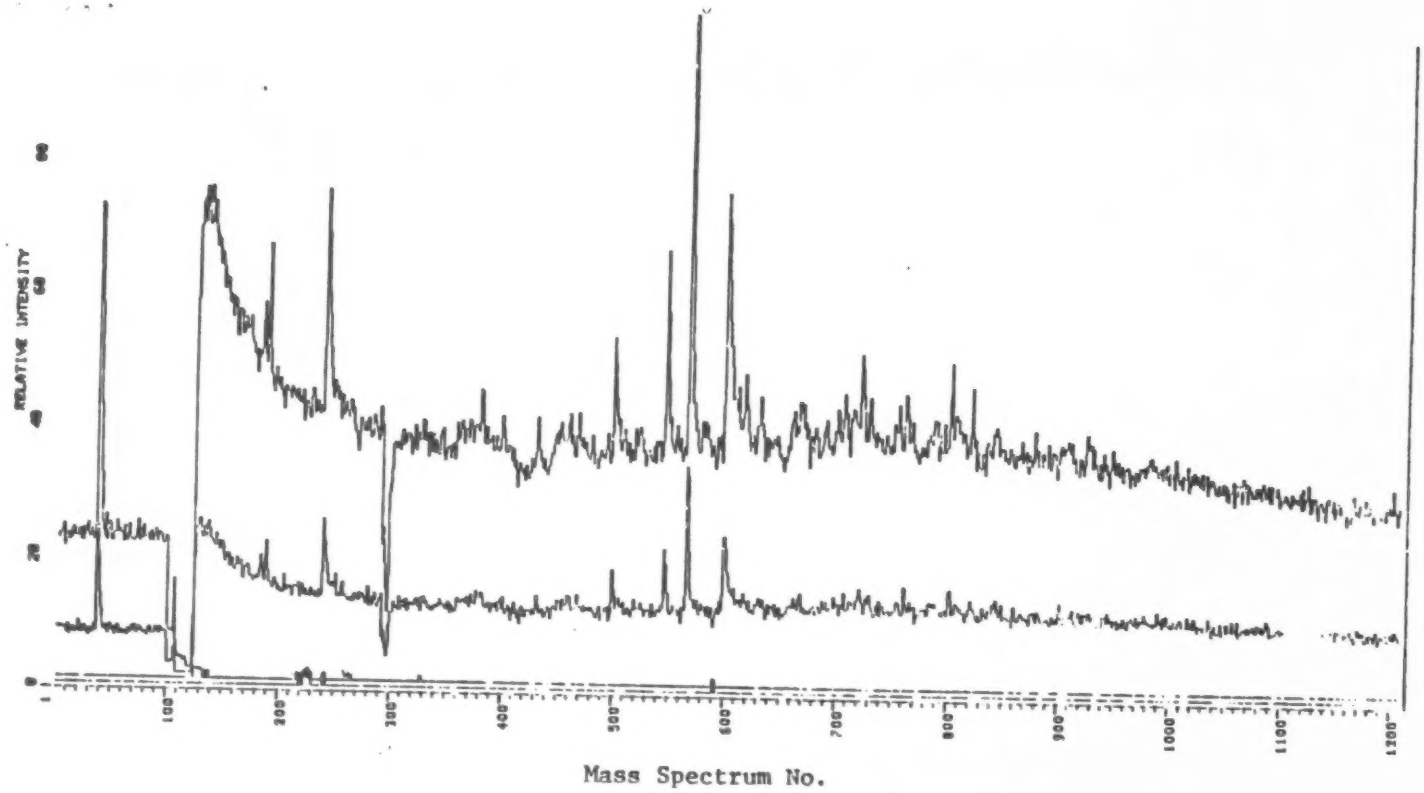

Figure A84. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) for Effluent No. 3 from superchlorination process.

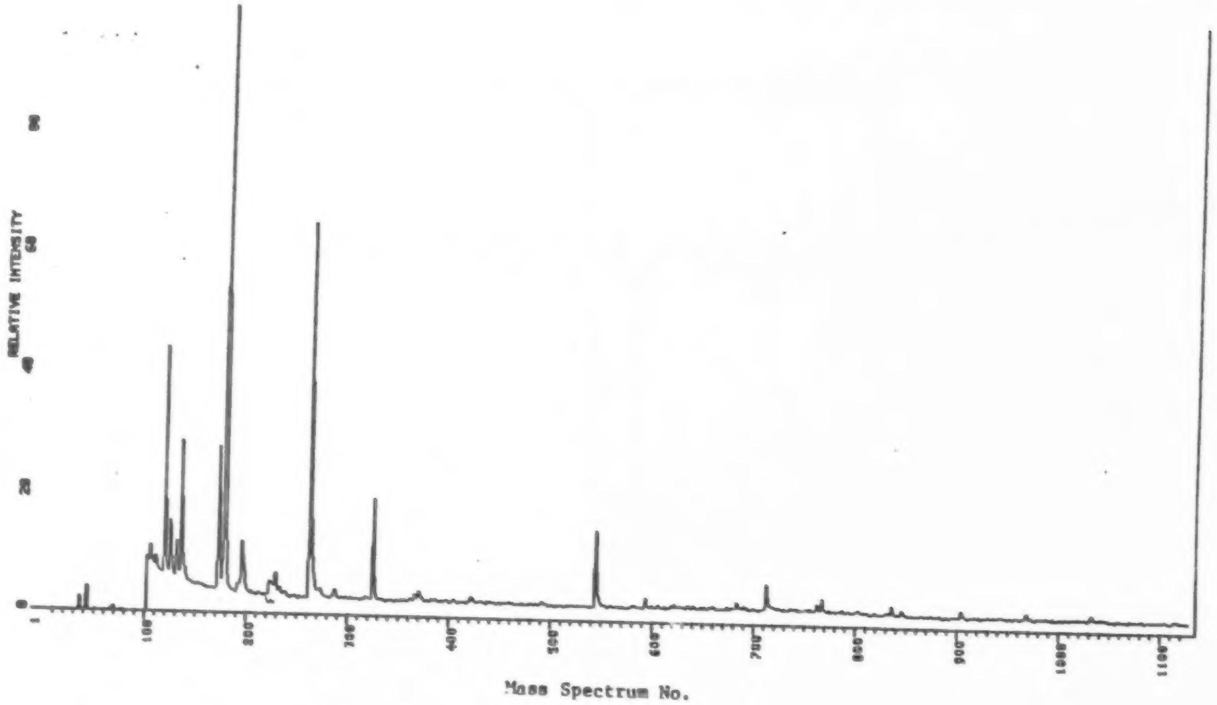

Figure A85. Electron impact GC/MS/COMP profile of GPA 1 "blank".

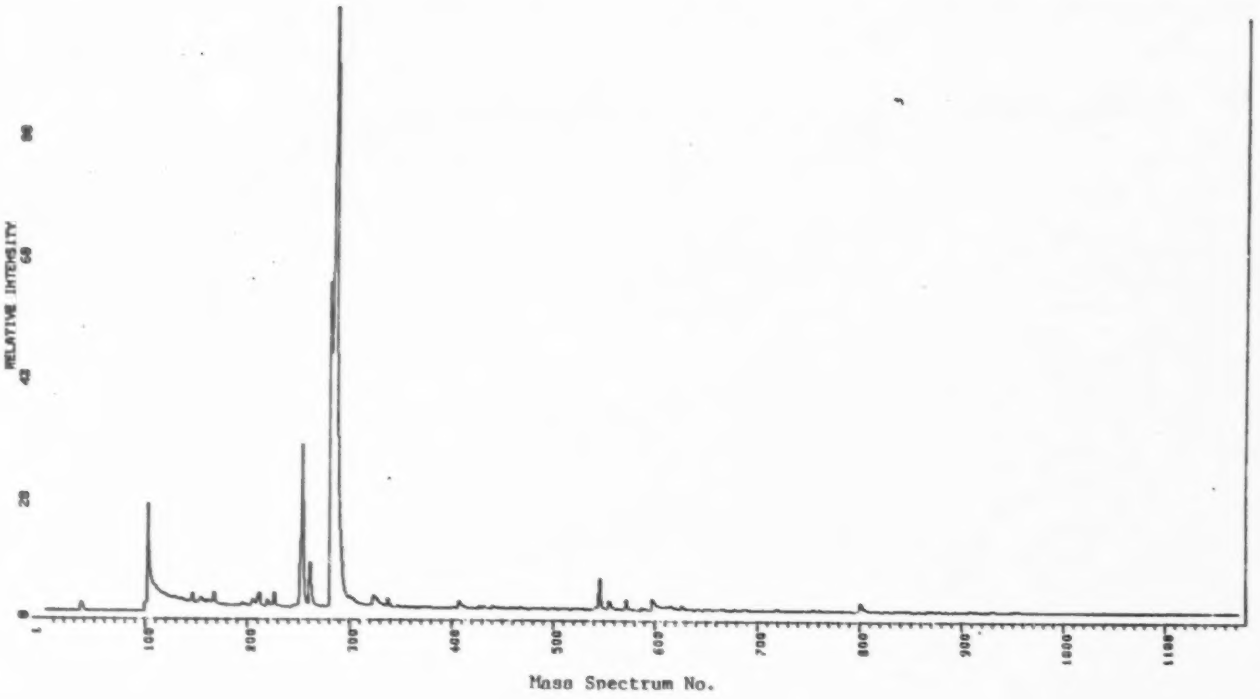

Figure A86. Negative chemical ionization GC/MS/COMP profile of GPA 1 for "blank".

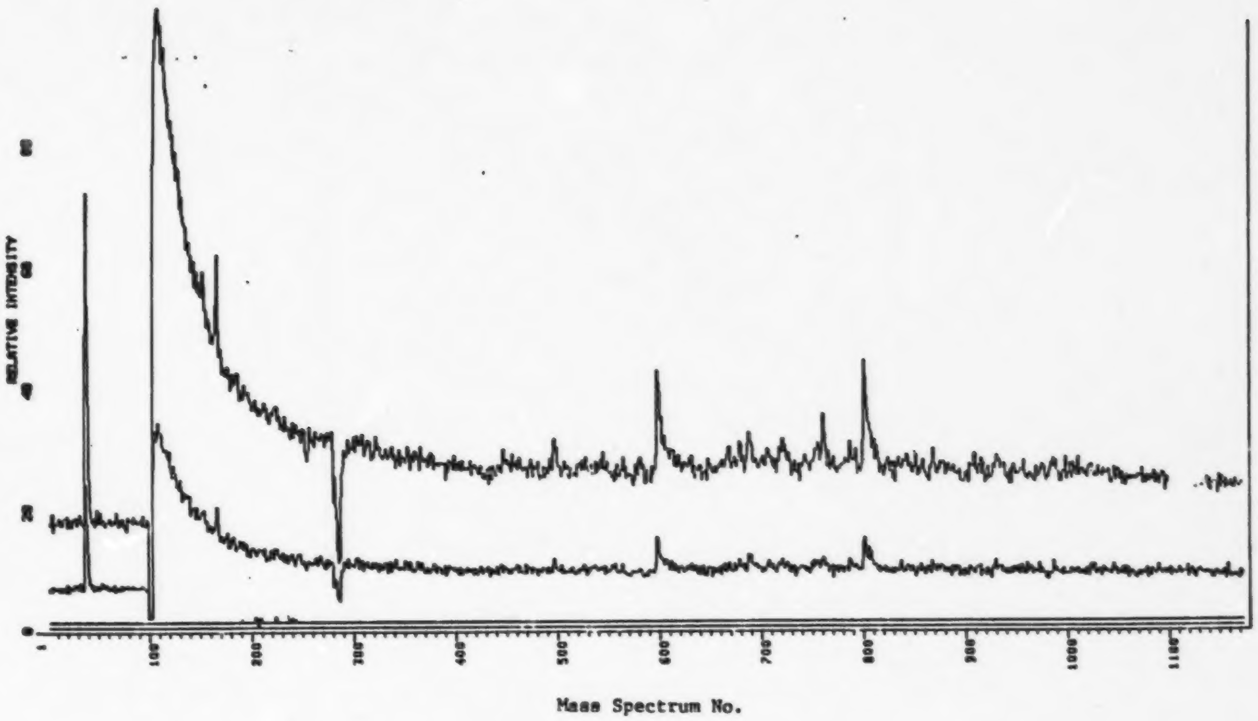

Figure A87. Negative chemical ionization GC/MS/COMP profiles (m/z 35, 37, 79, 81) of GPA 1 for "blank".

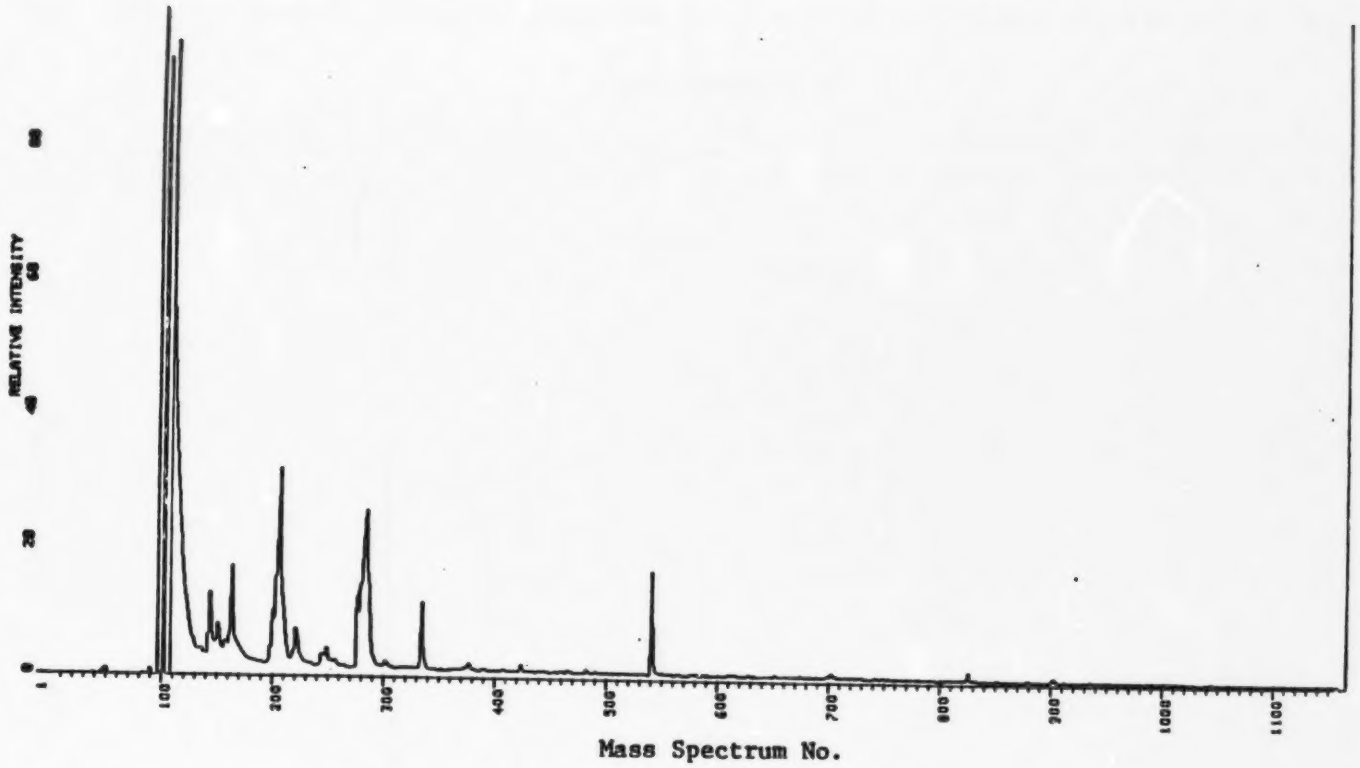

Figure A88. Electron impact GC/MS/COMP profile of GPA 4 fraction for Influent No. 2 from superchlorination process.

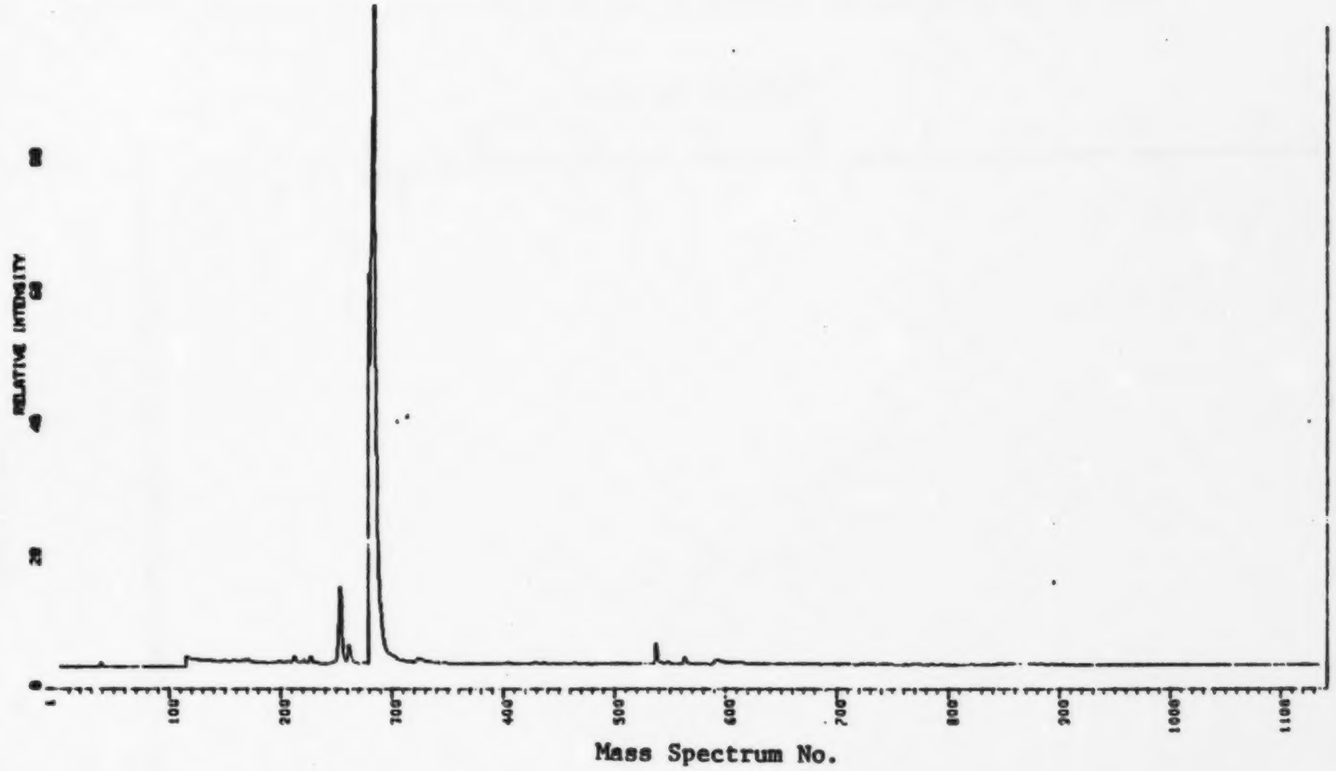

Figure A89. Negative chemical ionization GC/MS/COMP profile of GPA 4 fraction for Influent No. 2 from superchlorination process.

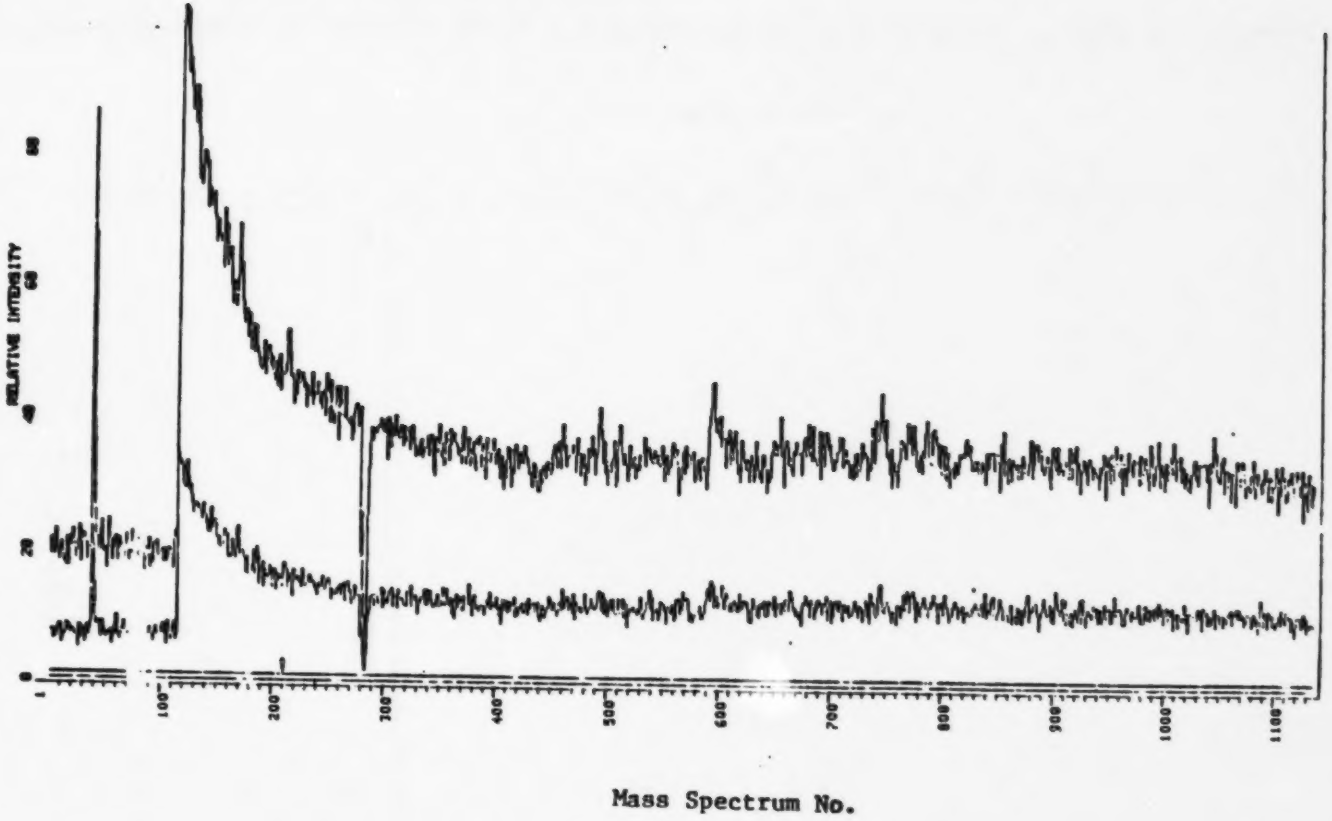

Figure A90. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GPA 4 fraction for Influent No. 2 from superchlorination process.

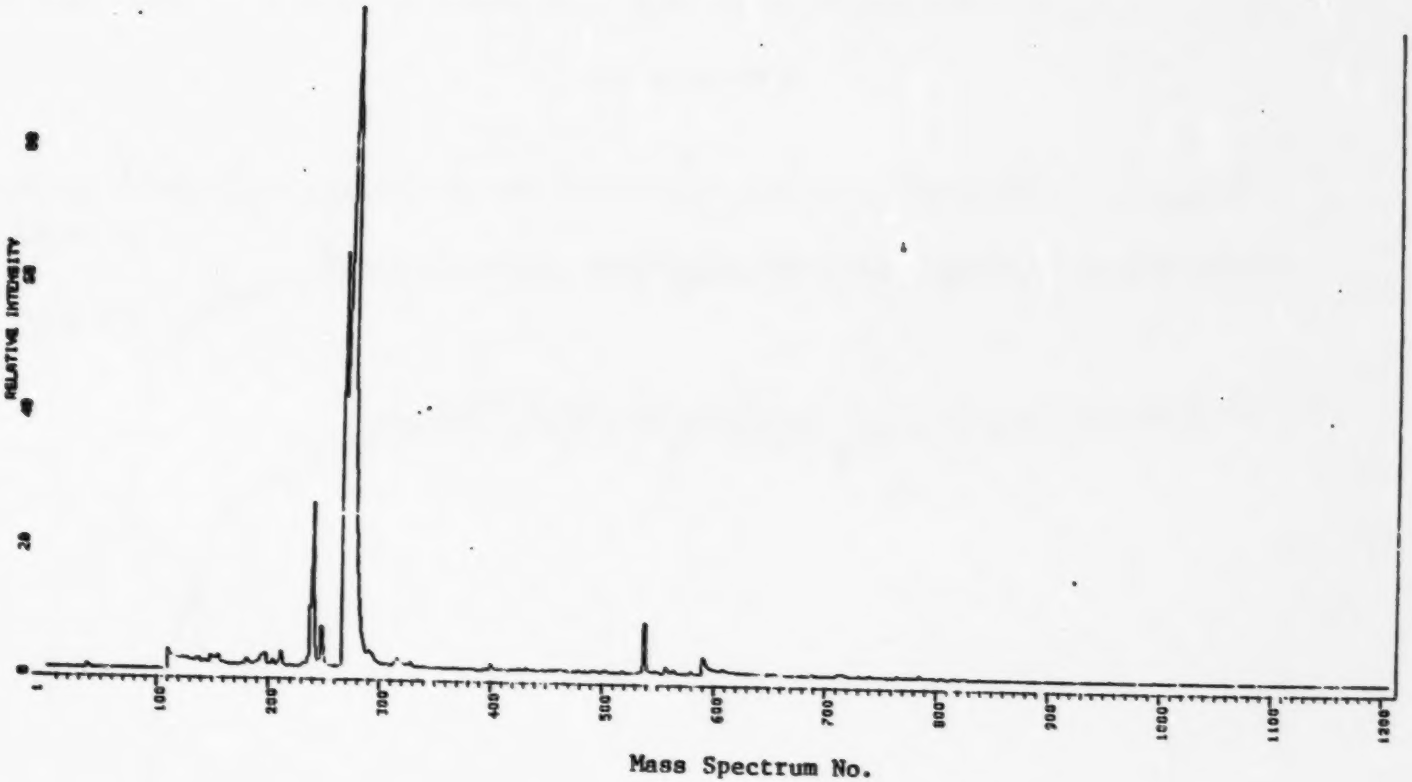

Figure A91. Negative chemical ionization GC/MS/COMP profile of GPA 4 fraction for Effluent No. 2 from superchlorination process.

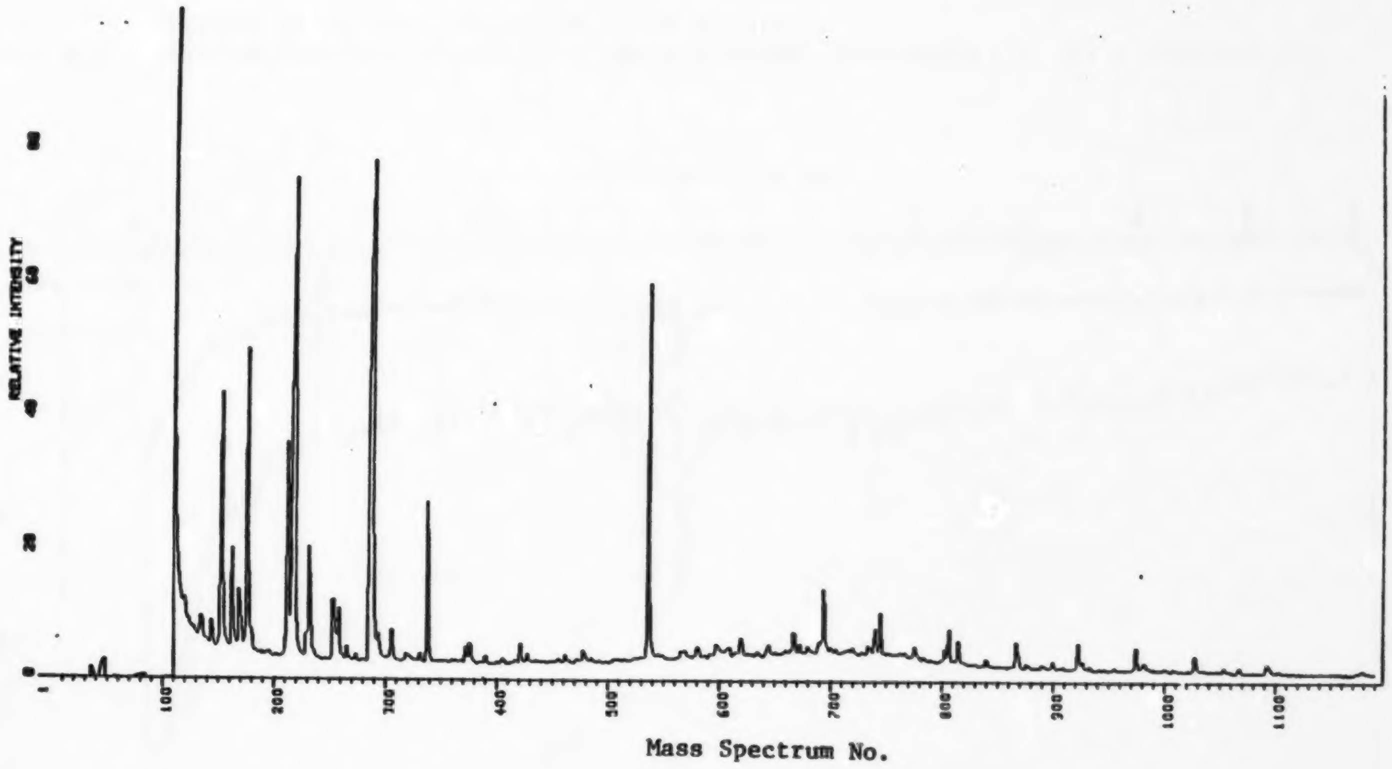

Figure A92. Electron impact GC/MS/COMP profile of GPA 4 for Effluent No. 2 from superchlorination process.

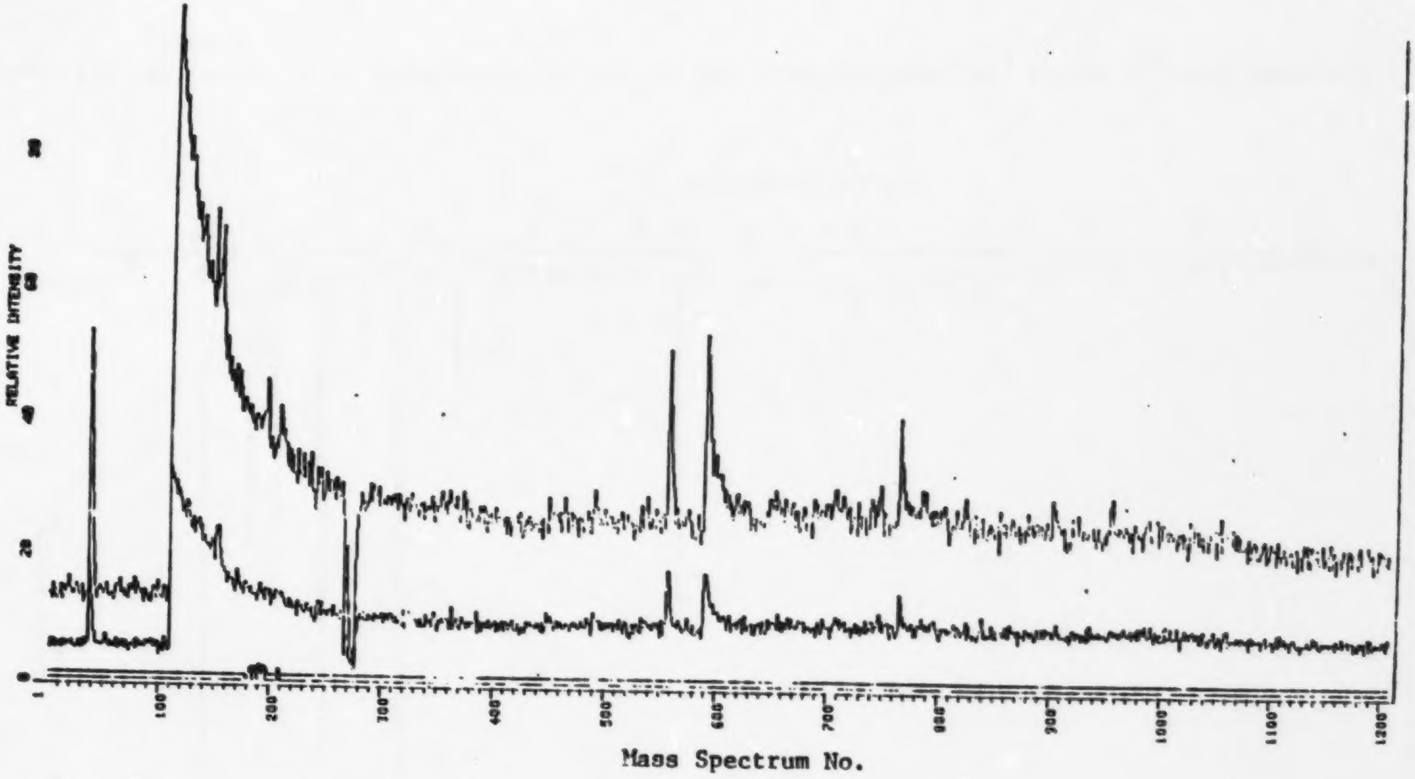

Figure A93. Negative chemical ionization GC/MS/COMP single ion profiles of GPA 4 fraction for Effluent No. 2 from superchlorination process.

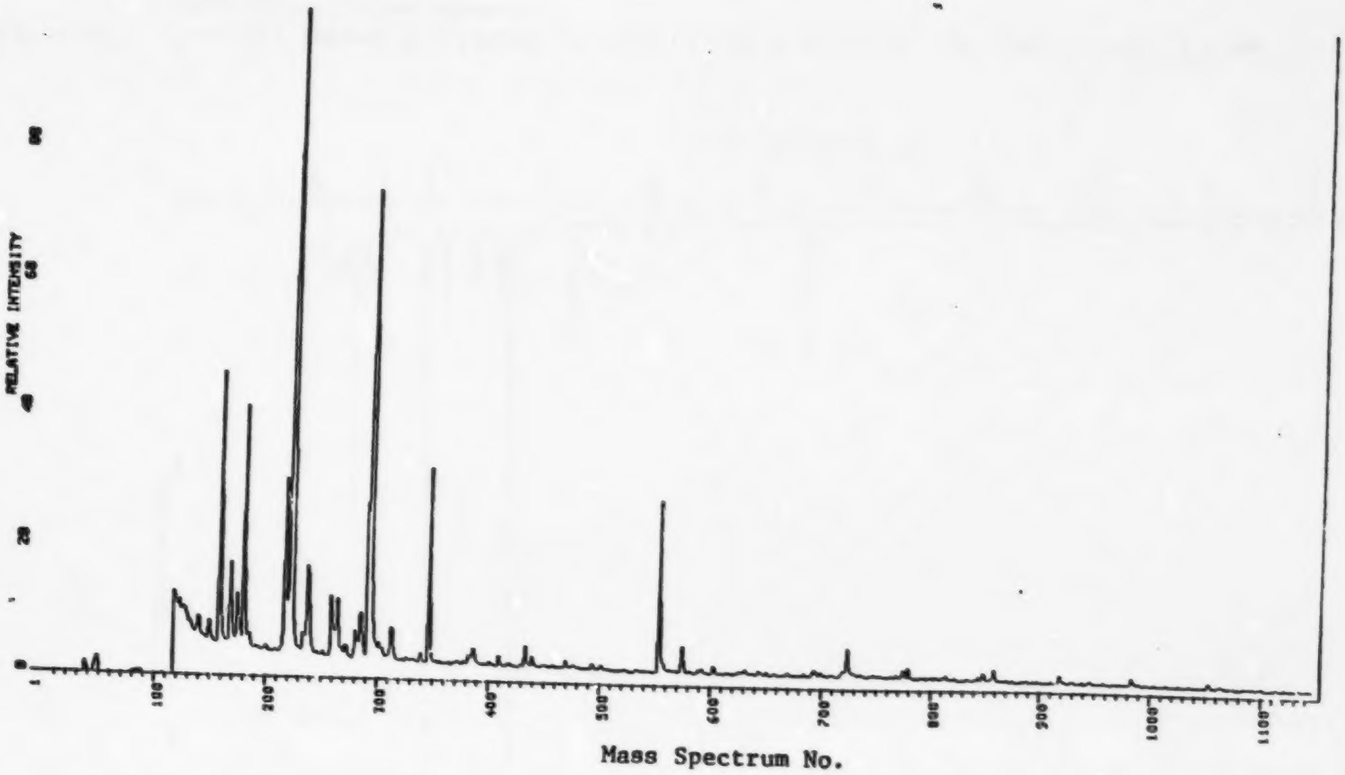

Figure A94. Electron impact GC/MS/COMP profile of GPA 4 fraction for Influent No. 3 from superchlorination process.

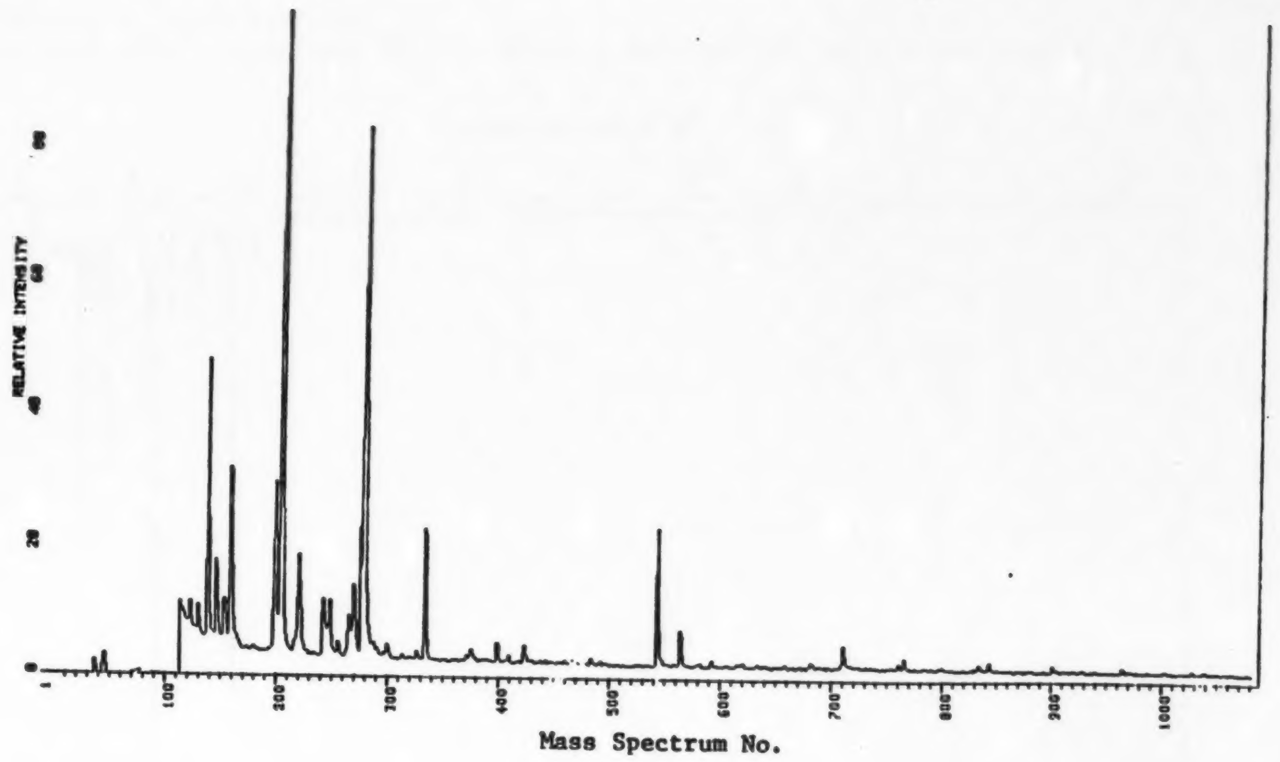

Figure A95. Electron impact GC/MS/COMP profile of GPA 4 fraction for Influent No. 3 from superchlorination process.

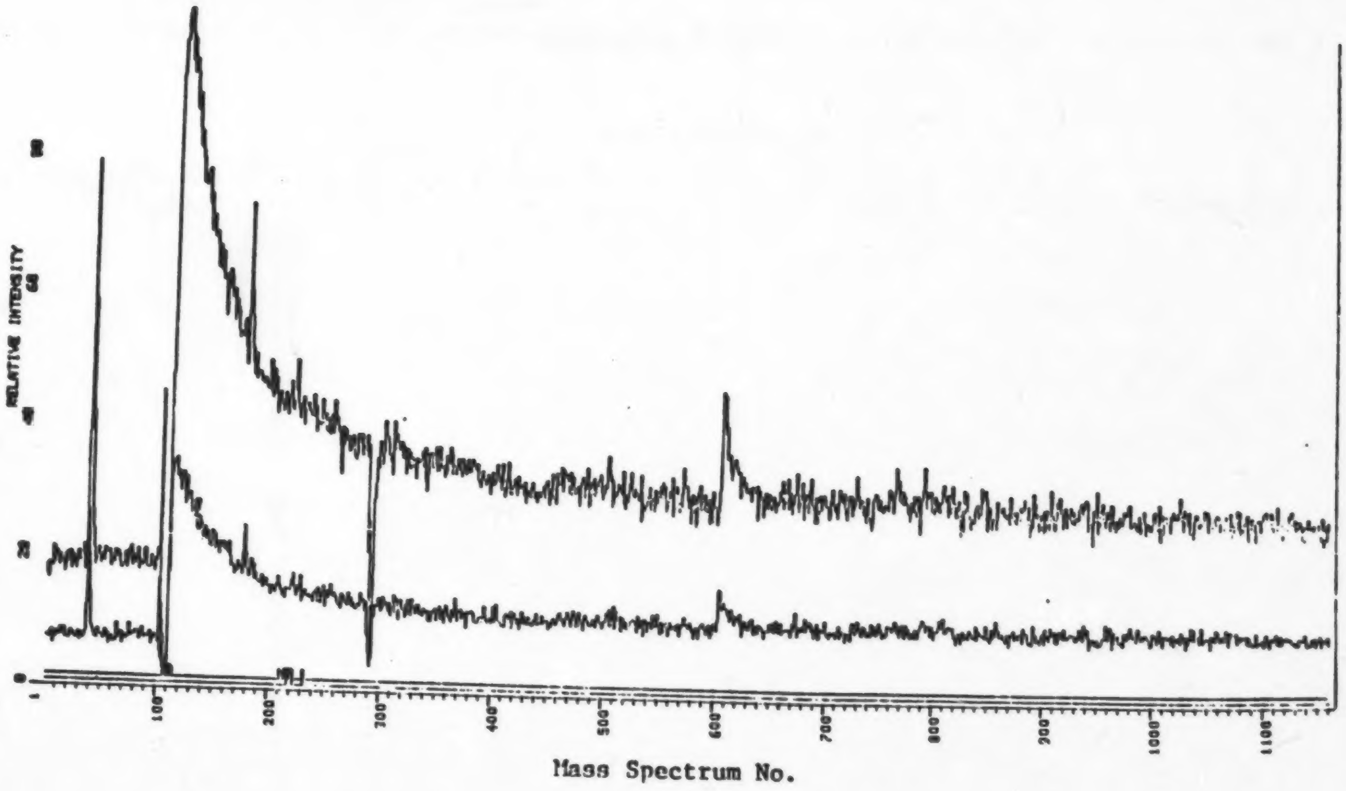

Figure A96. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GPA 4 fraction for Influent No. 3 from superchlorination process.

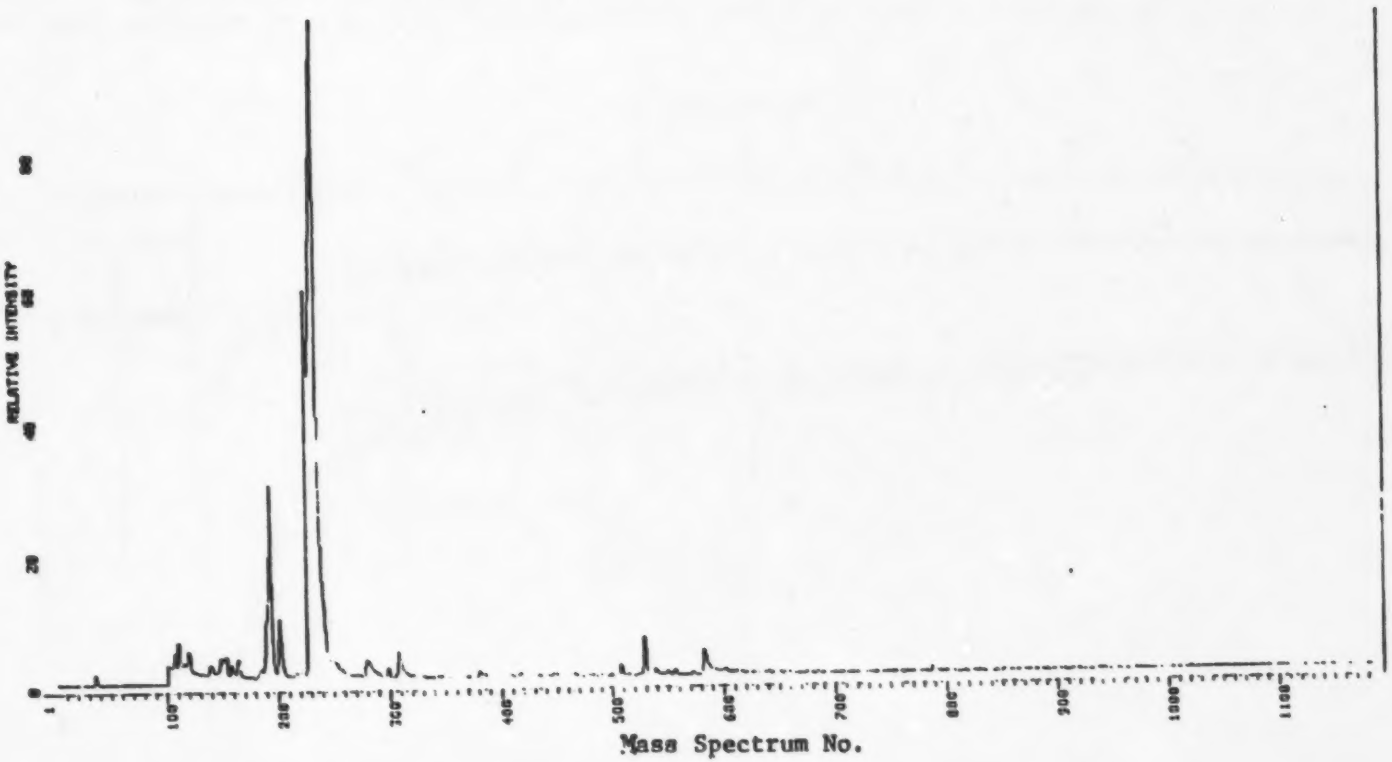

Figure A97. Negative chemical ionization GC/MS/COMP profile of GPA 4 fraction for Effluent No. 3 from superchlorination process.

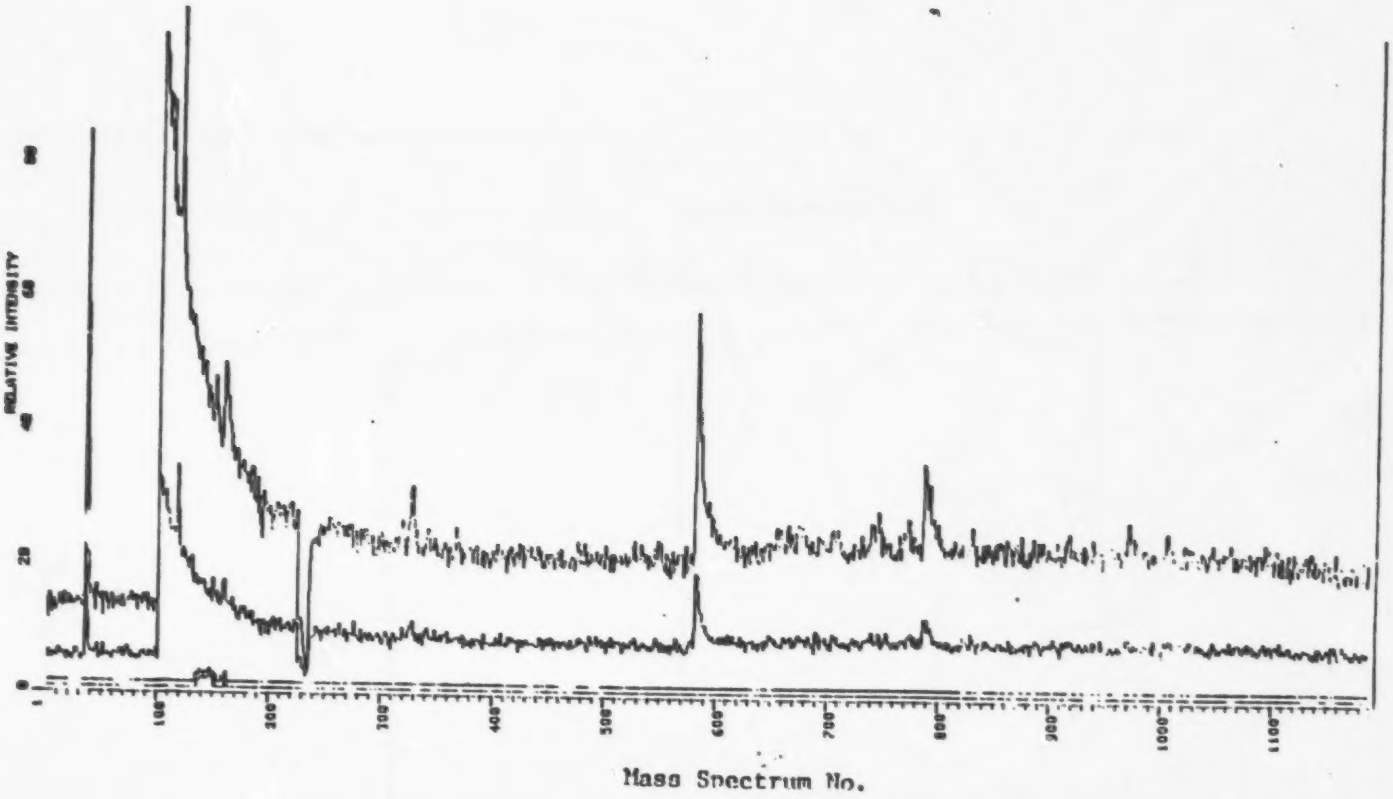

Figure A98. Negative chemical ionization GC/MS/COMP profile single ion profiles (m/z 35, 37, 79, 81) of GPA 4 fraction for Effluent No. 3 from superchlorination process.

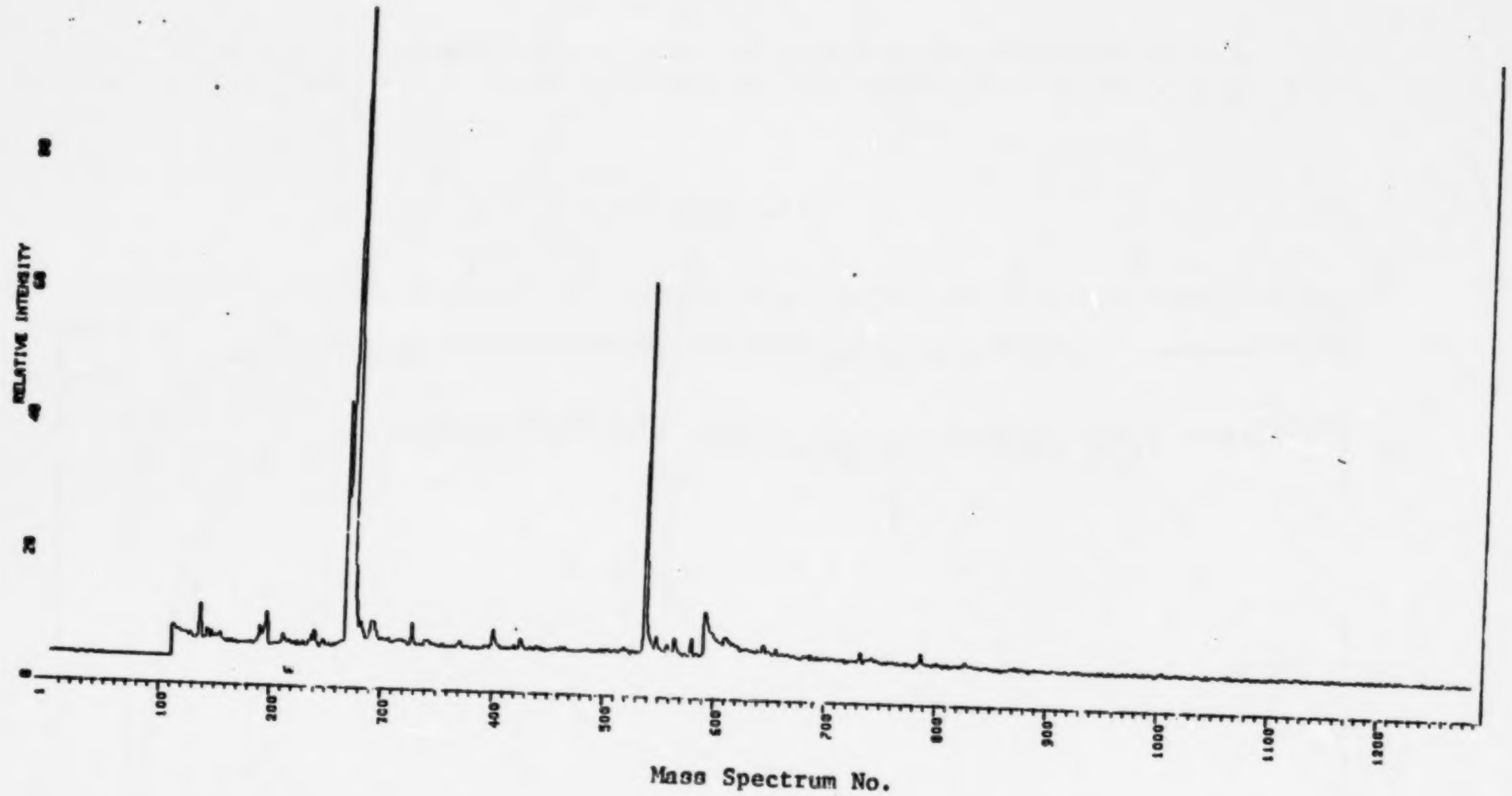

Figure A99. Negative chemical ionization GC/MS/COMP profile of GPA 4 "blank".

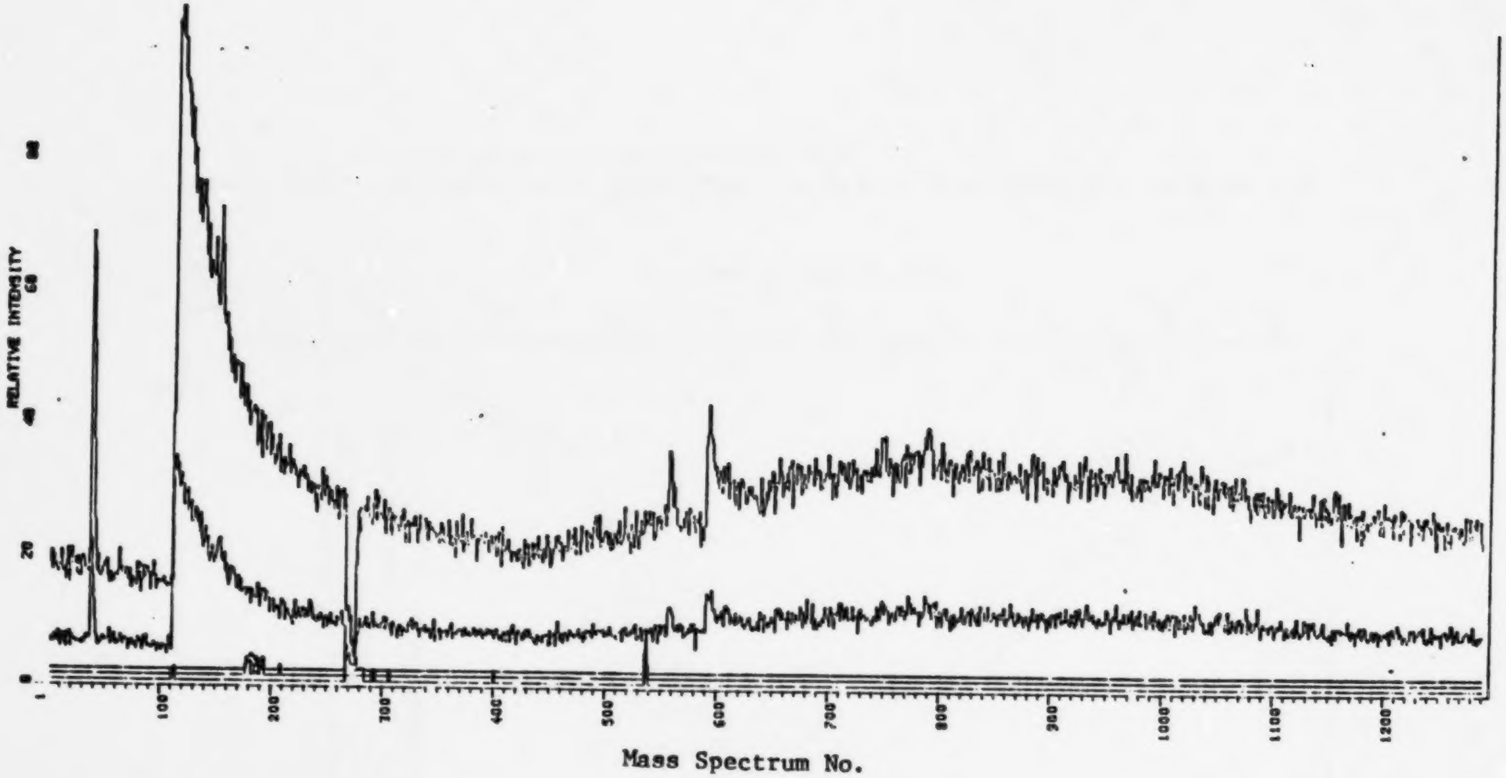

Figure A100. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of GPA 4 "blank".

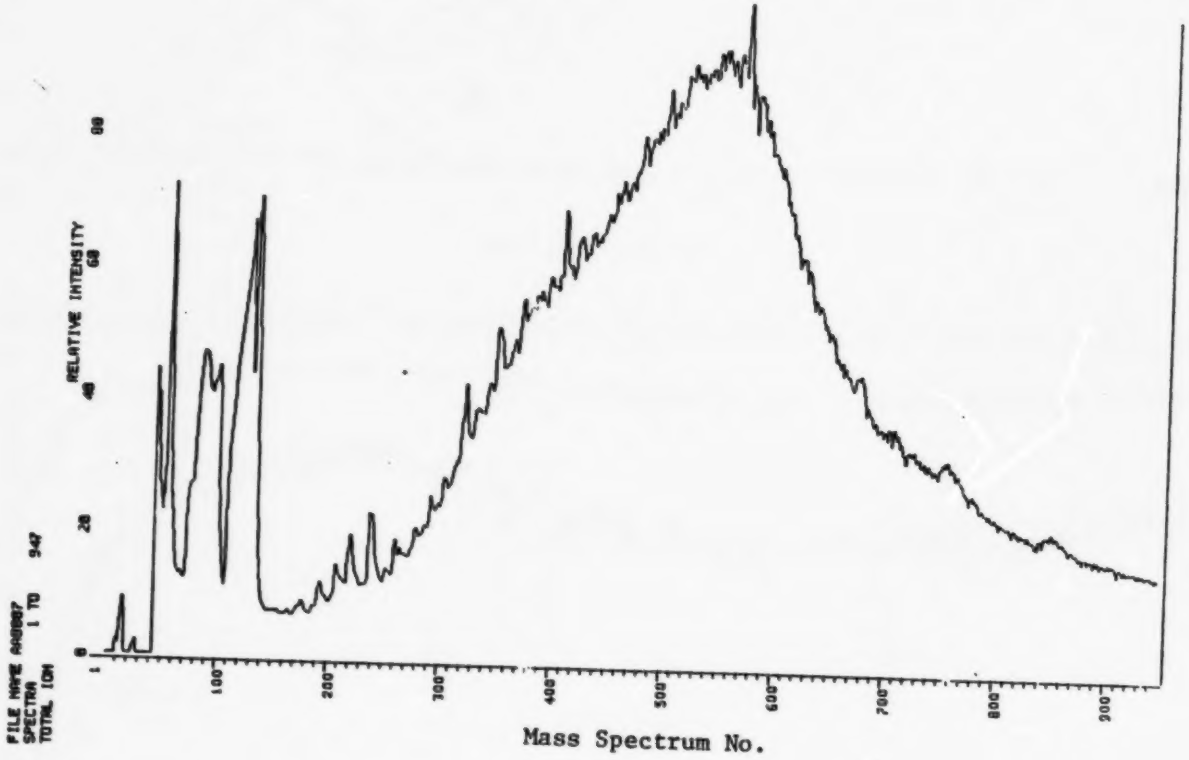

Figure A101. Electron impact GC/MS/COMP profile of S1-neutral THF fraction for Effluent No. 1 (SP2100 capillary).

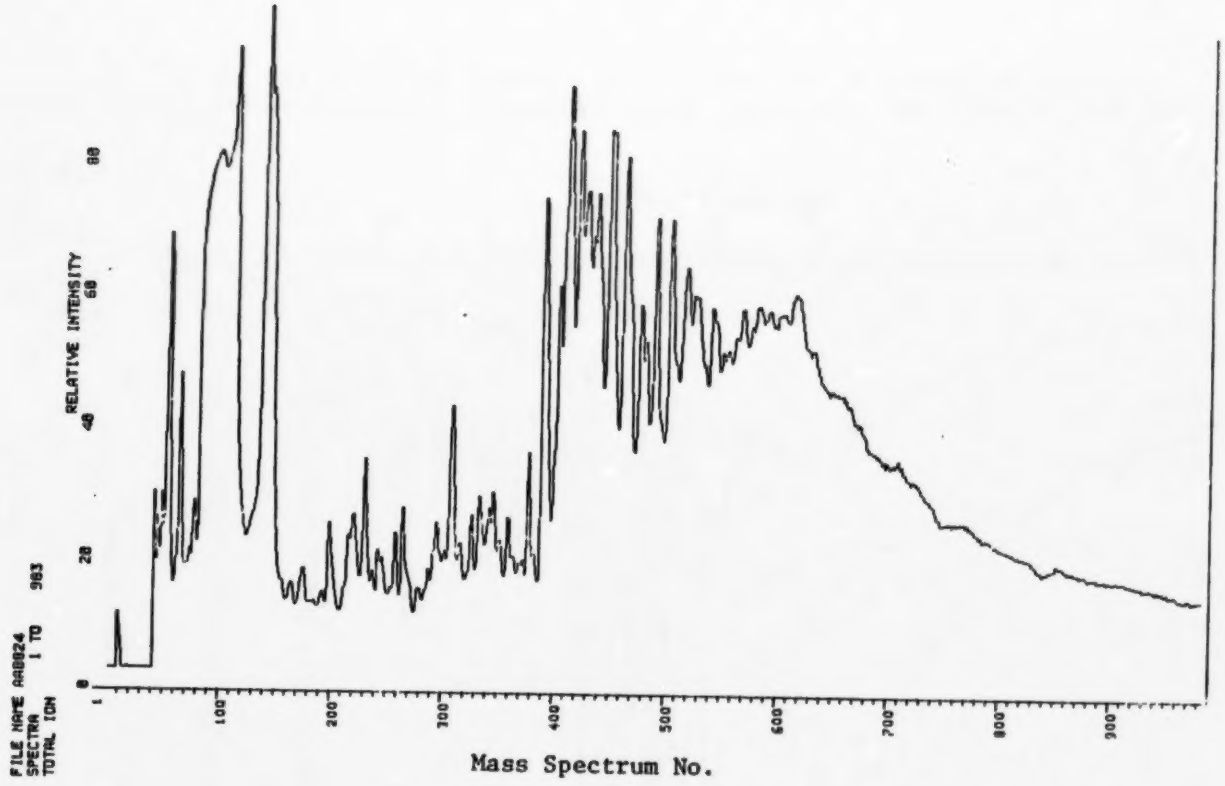

Figure A102. Negative chemical ionization GC/MS/COMP profile of S1-THF fraction for Effluent No. 1 (SP2100 capillary).

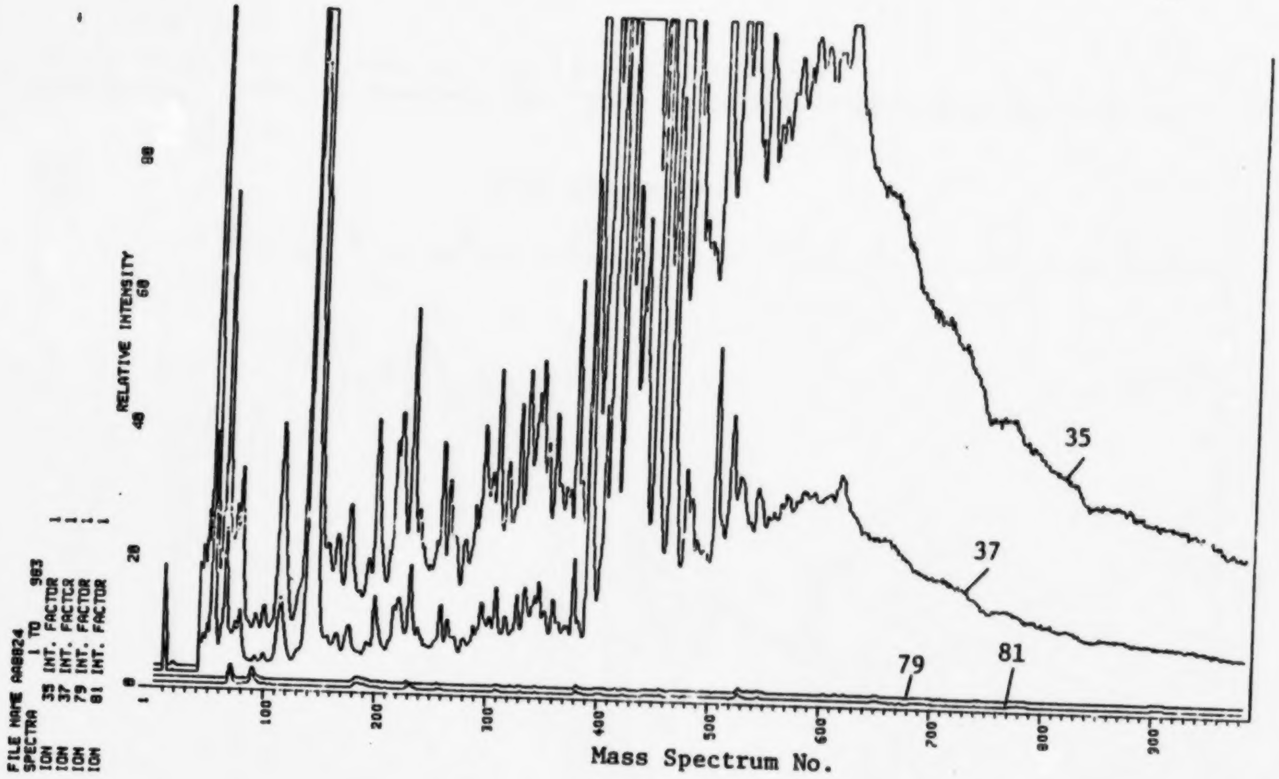

Figure A103. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of S1-THF fraction for Effluent No. 1 (SP2100 capillary).

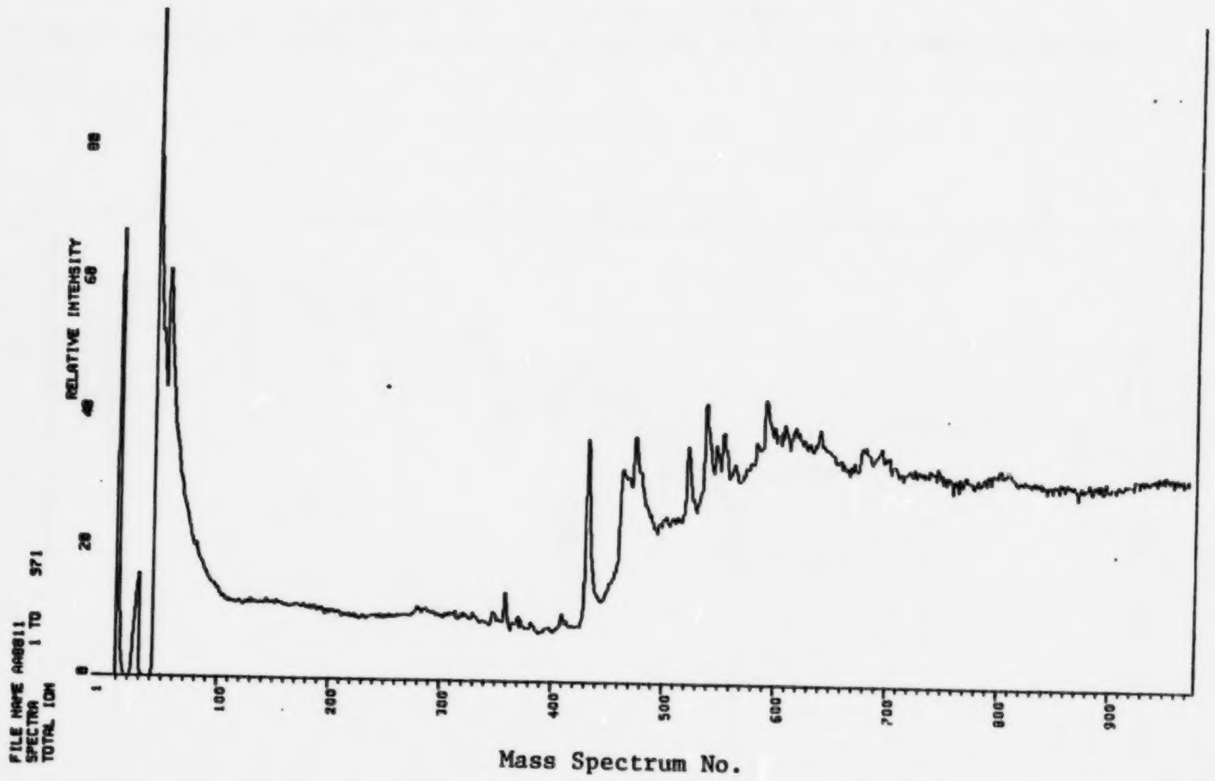

Figure A104. Electron impact GC/MS/COMP profile of S3-neutral acetone fraction of Effluent No. 1 (SP2100 capillary).

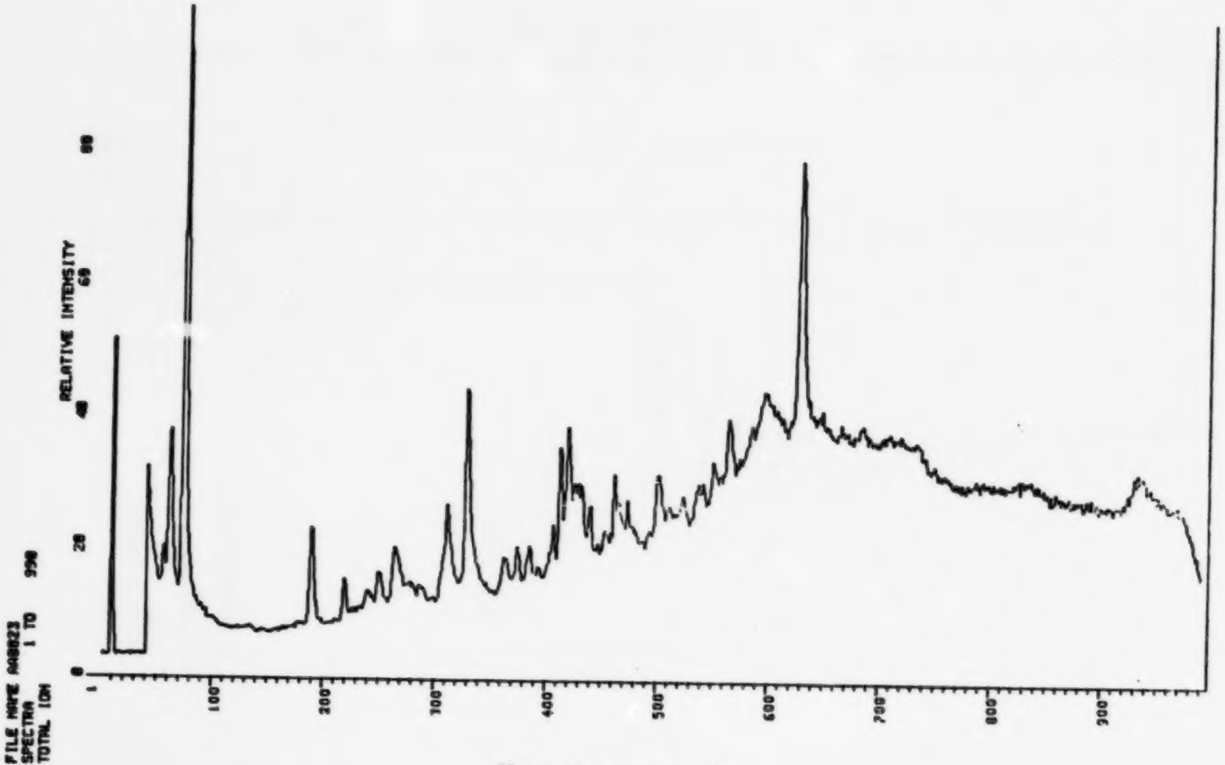

Figure A105. Negative chemical ionization GC/MS/COMP profile of S3-neutral acetone fraction for Effluent No. 1 (SP2100 capillary).

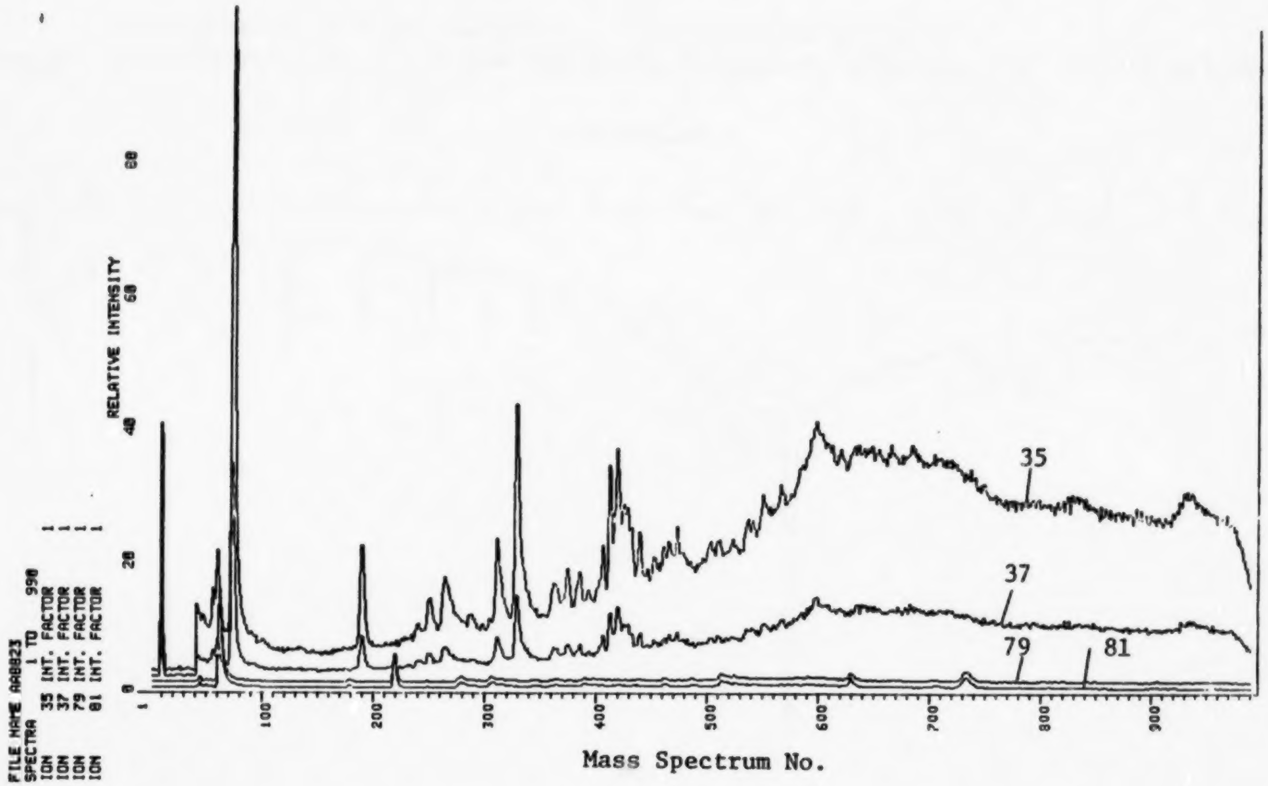

Figure A106. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of S3-neutral acetone fraction for Effluent No. 1 (SP2100 capillary).

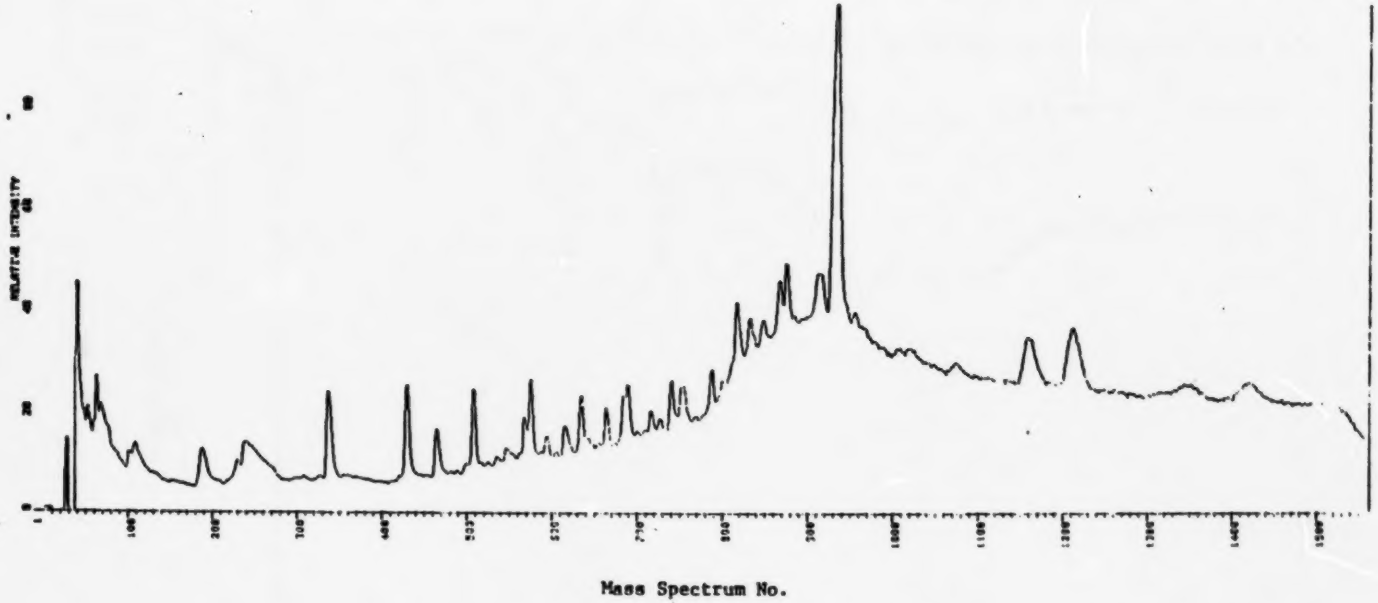

Figure A107. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction for Effluent No. 2 from superchlorination process (Cl_2 unquenched in sample).

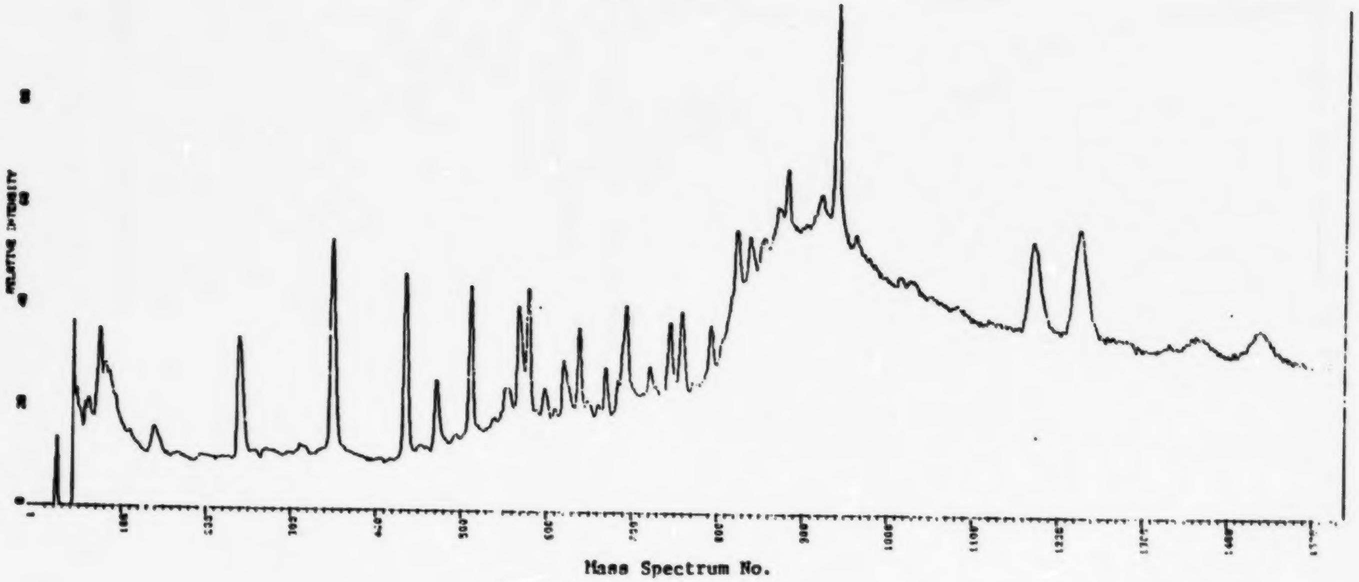

Figure A108. Negative chemical ionization GC/MS/COMP profile of "neutral" fraction for Effluent No. 2 from superchlorination process (Cl_2 quenched in sample).

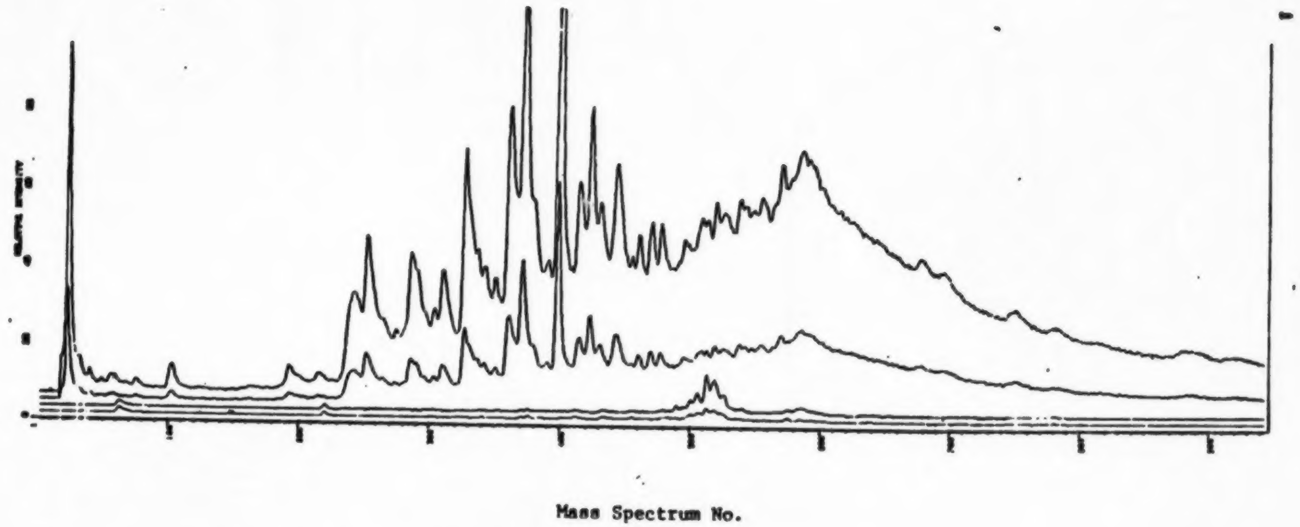

Figure A109. Negative chemical ionization GC/MS/COMP for ion profiles (m/z 35, 37, 79, 81) of "neutral" fraction for Effluent No. 2 from superchlorination process (Cl_2 quenched in sample).

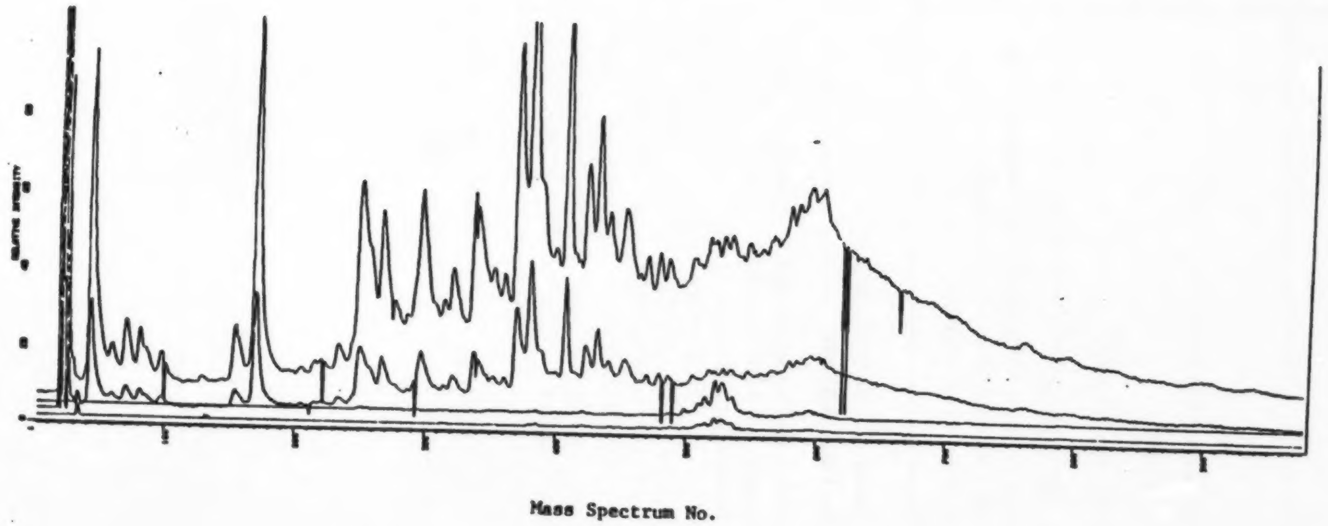

Figure A110. Negative chemical ionization GC/MS/COMP single ion profiles (m/z 35, 37, 79, 81) of "neutral" fraction for Effluent No. 2 from superchlorination process (Cl_2 in sample unquenched).